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# ***JPRS Report***

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***Central Eurasia:  
Chemistry***

# Science & Technology

## CENTRAL EURASIA: CHEMISTRY

JPRS-UCH-93-004

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25 February 1993

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**Quantum-Chemical Investigation of Active Centers of Cationic Polymerization of Olefines in Presence of Aluminum Halide Complexes With Proton Donors**

937M0077A Kiev *TEORETICHESKAYA I  
EKSPERIMENTALNAYA KHIMIYA in Russian*  
Vol 28 No 1, Jan-Feb 92 pp 12-20

[Article by K. S. Minsker, V. A. Babkin, Bashkir University, Ufa; UDC 541.64:547.25]

[Abstract] Aluminum halide complexes with proton donors can initiate cationic polymerization of olefines. By varying the nature of the proton donor, it is possible to obtain complexes with a wide range of activity and selectivity of the action. In this work, quantum chemical investigation of the interaction of  $R_nAlCl_{3-n} \cdot xH_2O(ROH)$  with olefines (ethylene, propylene and isobutylene) was carried out in an attempt to establish the mechanism of the formation of active centers by cationic polymerization and to determine their structures. It was shown that the formation of such active centers and their transformations occur only in presence of olefines. In all cases analyzed, coordination mechanisms of the initiation processes were observed which in the past were seen only in case of isobutylene in presence of  $AlCl_3$  aqua-complexes. In case of  $Al(C_2H_5)_2Cl_2(ROH)$ , regardless of the nature of the base, both proton donor and carbon-cationic activity was observed with formation of two types of active centers. The probability of either one being formed was the same in case of ethylaluminum dichloride - ethyl ether complexes. It is possible that this is a general phenomenon which should always be considered in analysis of experimental data. These data agree with other experimental and theoretical data. They could be used in deciding on regulation of the catalytic activity of such complexes. Tables 3; figures 4; references 13; 8 Russian, 5 Western (1 by Russian authors).

**-Electronic Hyperpolarizability of Even Polymers in Complete Configurational Interaction Method**

937M0077B Kiev *TEORETICHESKAYA I  
EKSPERIMENTALNAYA KHIMIYA in Russian*  
Vol 28 No 1, Jan-Feb 92 pp 21-25

[Article by Yu. F. Pedash, V. V. Ivanov, A. V. Luzanov, Kharkiv University; UDC 539.192]

[Abstract] Production of polymer materials with high non-linear optical perception created a non-trivial theoretical problem of determining the polarizability of higher order as a function of the length of the  $\pi$ -configuration in elongated molecular systems. The goal of this work was to determine the dependence of the  $\pi$ -component of the hyperpolarizability ( $\alpha^{(3)}$ ) on the length of conjugated chain in even polyenes using the  $\pi$ -electronic method - the method of complete configurational interaction (CCI) of all possible  $\pi$ -states. The calculations were done by the final field method. In the CCI and in the limited Hartree-Fock models the polarizabilities could be calculated on the basis of respective derivatives along the field related to energy or to

the dipole moment induced by the field. Formulas were developed for  $\alpha^{(3)}$  which indicated the principal role of electronic configuration in calculations of hyperpolarization of elongated  $\pi$ -electronic systems on one hand and, on the other hand, allowed to evaluate the increase of  $\alpha^{(3)}$  with an increase in the conjugated system in the polyene chains. It was shown that the second hyperpolarizability of  $C_{2N+2}$  polyenes ( $N=2-10$ ) increased as  $N^{3.45}$  in the restricted Hartree-Fock method. Table 1; references 9; 6 Russian, 3 Western.

**Hyperpolarizability of Polyene Chains in Hückel Model With Consideration of Real Geometry**

937M0077C Kiev *TEORETICHESKAYA I  
EKSPERIMENTALNAYA KHIMIYA in Russian*  
Vol 28 No 1, Jan-Feb 92 pp 25-29

[Article by Yu. F. Pedash, A. Yu. Semenov, Kharkiv University; UDC 539.192]

[Abstract] The goal of this work was to explain the relationship between average  $\gamma$  value (Hückel hyperpolarizability of  $\pi$ -electrons) and the length of conjugated chain with consideration of all components in two configurations of polyene chains (cis and trans) and to investigate the effect of alternating bond length of this function. It was shown that with an increased degree of alternation (decreased  $N_d$ ) the  $\gamma$  value decreased faster in the cis configured structures. Significant differences were noted between the  $\gamma$ -values of cis- and trans- forms with identical  $N$  and  $N_d$ ; as  $N$  increased, the  $\gamma$  values tended towards different limits. Strong dependence of  $\gamma$  on geometric parameters of the polyene chains was noted. The  $\pi$ -electron hyperpolarizability of trans-polyenes diminished to zero at a C-C-C bond angle of  $125^\circ$ . The signs of the cis-polyene  $\gamma$ -values alternated, depending on the evenness of  $N/2$  ( $N$  = number of C atoms). The approximate functions were established for the trans ( $\gamma \approx N^5$ ) and cis-form ( $\gamma \approx N^6$ ) of the polyenes. Tables 2; references 9; 3 Russian (2 by Western authors), 6 Western.

**Quantum-Chemical Study of Hydrogen Bonding in Ice Forming Reagents Complexed With Water**

937M0077D Kiev *TEORETICHESKAYA I  
EKSPERIMENTALNAYA KHIMIYA in Russian*  
Vol 28 No 1, Jan-Feb 92 pp 41-47

[Article by V. K. Yatsimirskiy, L. P. Oleksenko, A. V. Arkhapov, Kiev University; UDC 541.123.22 + 536.421.4]

[Abstract] In an attempt to establish correlations between ice forming activity of organic reagents and the hydrogen bonding parameters, three reagents were investigated by the MNDO method: 1,3,5-trihydroxybenzene and 1,5- and 2,6-dihydroxy naphthalene (DHN), the last reagent being used as a control because it is not an ice forming compound. Quantum-chemical calculations

were performed of the electron structure of the complexes  $IR...H_2O$  and  $IR...2 H_2O$  ( $IR$  = ice forming reagents) with complete optimization of their geometry. It was shown that such complexes did form and an alternation of positive and negative charges was observed both in the ice forming reagents and in water molecules. The low ice forming activity of 2,6-DHN was explained by the absence of "cooperative" hydrogen bonds observed in ice crystals, in 1,3,5-trihydroxybenzene and in 1,5-DHN. The results obtained were compared with literature data on ice forming activity and structural characteristics of the investigated  $IR$  crystals. Tables 4; figure 1; references 12: 7 Russian, 5 Western.

### Transformations of Organoaerosilanes Affected by Ionizing Radiation

937M0077E Kiev *TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 28 No 1, Jan-Feb 92 pp 72-77*

[Article by Ye. G. Yevtushenko S. T. Yankova, M. M. Aleksankin, I. P. Samchenko, V. P. Fordiyenko, Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, Academy of Sciences of Ukraine, Kiev; UDC 541.15:541.183]

[Abstract] Earlier studies have shown that aerosilanes with allyl or phenyl groups grafted on the surface of polyethylene are capable of forming spacial networks upon exposure to ionizing radiation. This could result in significantly improved thermal-mechanical properties of such compositions. The goal of this work was to investigate radiolysis of allylhydroxyaerosilane (AHA) and diphenylaerosilane (DPA) obtained from aerosilane A-300. Physical properties were determined by EPR, mass spectrometry and IR-spectroscopy. It was discovered that the yields and the types of free radicals obtained corresponded to what one would expect from individual components of the products obtained. In irradiated AHA several compounds were detected resulting from hydrogenation of the allylic groups. A 1 MHz irradiation dose of DPA showed no significant changes in the IR or EPR spectra, indicating that the surface grafted phenyl groups were radiologically stable. Table 1; figures 2; references 13: 10 Russian, 3 Western.

### Transformation of Ethanol During Thermolysis of Dyes Adsorbed on Silicon Surface

937M0077F Kiev *TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 28 No 1, Jan-Feb 92 pp 87-91*

[Article by O. I. Kozik, I. M. Gavriluk, V. A. Pokrovskiy, A. A. Chuyko, Institute of Surface Chemistry, Academy of Sciences of Ukraine, Kiev; UDC 541.183:543.226:547.869:541.129:546.11:543.42]

[Abstract] Individual sorption of alcohols on the surface of dispersed silicon is characterized by formation of

adsorption complexes with active centers at the surface. Chemosorption of alcohol molecules may occur by the mechanisms of: electrophilic substitution of the surface OH group protons, by nucleophilic substitution of surface hydroxyl groups or by an interaction with siloxane "bridges" with an addition of a molecule. In present work, the role of adsorbed solvent and the transformation of its molecules during the thermolysis and thermal desorption of heteroatomic dyes was investigated. Studying the system quinoline-ethanol-silica gel showed that thermal behavior of the adsorbed form of the solvent resembled the pattern seen in aerosilane. At 370 K thermal evolution of weakly bound solvent takes place followed by isolation of quinoline at 410 K; the tightly bound ethanol forms break down at higher temperatures. This pattern fits the concepts of the nature of active surface centers in dispersed silicon oxide and indicates ethoxylation of the surface at elevated temperatures. Presence of small quantities of aromatic molecules on the surface has shown no effect on the kinetics of individual desorption and thermal conversions of alcohol molecules. The reaction of dye and ethanol molecules with the surface layer is manifested only as a complex formation in the excited state which stimulates adsorption of the solvent during the breakdown of the complex. Figures 2; references: 11 (Russian).

### Sorption-Photometric Determination of Cobalt Using Modified Silica Gel

937M0138C Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 58 No 11, Nov 92 (manuscript received 22 Jun 92) pp 990-994*

[Article by V. V. Sukhan, L. I. Savranskiy, O. A. Zaporozhets, O. Yu. Nadzhafova, and G. V. Lantukh, Colloidal Chemistry and Hydrochemistry Institute, Kiev; UDC 543.31:543.42:543.544:546.732]

[Abstract] Modified silica gels have the advantages of mineral-based sorbents (no swelling in solvents, chemical and mechanical stability, high rates of mass exchange) combined with the possibility of fixing an active component on the surface. Sorbents are modified by chemical or surfactant interaction with solutions. The latter method simplifies sorbent modification while retaining high sorption efficiency. It is well known that a "substance-on-carrier" system frequently becomes an entirely new material having properties different from either the sorbed substance or the carrier, opening the door to a number of new analytical procedures. In the present work the sorption of cobalt thiocyanate complex in static and dynamic modes on silica gel modified with didecylaminoethyl- $\beta$ -tridecylammonium iodide was studied. The sorption coefficient had a value of  $(2-5) \times 10^5$  ml per gram. Maximum sorption capacity for cobalt was  $2.5 \times 10^{-1}$  mmole per gram. The effects of interfering ions were investigated and a sorption-photometric method for the determination of cobalt in natural and potable waters with sensitivity limit of 1 microgram per liter was developed. Figure 1; references 2 (Russian).



**Extraction-Photometric Determination of Total Nickel Content in Waste Effluents**

937M0138D Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 58 No 11, Nov 92 (manuscript received 22 Jun 92) pp 995-996

[Article by V. V. Sukhan, V. F. Gorlach, B. I. Nabivanets, A. K. Boryak, and G. M. Slobodyanyuk, Kiev State University imeni T. G. Shevchenko; UDC 542.61]

[Abstract] The determination of total nickel content in waste waters is encumbered by its tying up with organic substances of complex, indefinite, and variable compositions. This causes the standard dimethylglyoximate method to give low readings with poor reproducibility. Other methods, such as atomic absorption, are also unsuitable. In the present work an extraction-photometric method based on the metal-benzylamine-dimethylglyoxime complex was developed. The influence of organic substances is overcome by preliminary treatment of the sample with hydrogen peroxide, nitric and sulfuric acids. Manganese and iron do not interfere with the determination in amounts below 2.5 grams per liter. References 6 (Russian).

**Effects of Fulvic and Humic Acids on Determination of Organic Forms of Mercury in Natural Fresh Waters by Non-Flame Atom-Absorption Method**

937M0141A Kiev KHIMIYA I TEKHOLOGIY VODY in Russian Vol 14 No 12, Dec 92 (manuscript received 17 Mar 92) pp 899-903

[Article by V. P. Antonovich, M. M. Novoselova, I. V. Bezlutskaya, and V. N. Krasnyukov, Physical Chemistry Institute, Odessa; UDC 543.3:546.49:547.992.2]

[Abstract] The effects of pH, sample storage time, and the presence of fulvic and humic acids on the behavior and determination of inorganic mercury by the "cold pair" method were studied previously and an analytical scheme was presented for natural fresh waters which takes these factors into account. For the purpose of ascertaining the feasibility of determining organic forms of mercury, a study was made of the behavior of methyl

and ethyl forms of mercury, i.e. the prime representatives of mercury-organic compounds in natural waters in the presence of river and soil humic and fulvic acids. It was demonstrated that it is possible for organic forms of mercury to interact with the humic compounds present in natural waters. Therefore, organic forms of mercury, while in the presence of fulvic and humic acids, are determined in a sulfuric acid medium with hydrazine borane. Figures 2, references 8: 6 Russian, 2 Western.

**Extraction-Atom-Absorption Determination of Indium in Waste Effluents**

937M0141B Kiev KHIMIYA I TEKHOLOGIY VODY in Russian Vol 14 No 12, Dec 92 (manuscript received 2 Jan 92) pp 903-906

[Article by A. A. Kroik, Dnepropetrovsk State University imeni 300th Anniversary of the Union of the Ukraine and Russian; UDC 543.070]

[Abstract] The determination of micro quantities of indium in waste effluents is needed since indium is a toxic micro-element similar in action to thallium. Atom-absorption spectrometry is not sensitive enough for direct determination of indium, although atom absorption combined with concentration by extraction increases the sensitivity of the determination. While extraction-atom-absorption techniques for indium using neutral extractants are known, they are unsuitable owing to the fact that as a rule the extraction must be carried out from solutions of halogen acids with the halide ion entering the organic phase and significantly lowering the strength of the indium atom-absorption signal. Also, these methods are not sufficiently sensitive and selective in water analysis. In the present work a method is presented for indium determination that is based on the preliminary conversion of indium into a complex compound prior to extraction with a solution of 8-mercaptoquinoline in amyl acetate. The indium is determined in the extract by atom-absorption spectrometry in an acetylene-air flame. The method is more selective than other methods in the presence of interfering components such as lead, zinc, iron, nickel, bismuth, vanadium, or molybdenum, and 7-10 times more sensitive than existing atom-absorption methods. The method is recommended for use in environmental protection and production control. References 4: 3 Russian, 1 Western.

### Catalytic Saponification of Vegetable Oil With Charcoal Enterosorbents

937M0076B Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 58 No 2, Feb 92 (manuscript received 10 Oct 90) pp 165-168

[Article by S. S. Stavitskaya, V. I. Davydov, S. G. Korvyakov, Division of Sorption and Fine Inorganic Synthesis, Institute of General and Inorganic Chemistry UkSSR Academy of Sciences, Kiev; UDC 541.128:541.183]

[Abstract] Carbon catalysts are very effective in acid-base reactions; the goal of this work was to determine whether the carbon containing enterosorbents used in medical applications could catalyze processes occurring in the organism, processes such as fat saponification. Catalytic properties of a series of enterosorbents were evaluated during saponification of vegetable (soy bean) oil under conditions approximating those existing in human organism. It was shown that charcoal sorbents (SKN and KAU type) effectively accelerated the saponification of soy bean oil, the rate of hydrolysis depending on the temperature and chemical nature of the surface of the charcoal catalyst. Modification of the charcoal surface with metal cations increased the rate of saponification in the order:  $Mg, K < Zn < Cr, Mn < Fe < Co < Ni < Cu$ . Hence, it was shown that sorption detoxification with charcoal may be accompanied by catalytic conversions of the fats leading to the formation of basic sources of human energy. This catalytic function must be considered when applying enterosorbents for the purpose of detoxification. Table 1; figures 3; references 11: 10 Russian (1 by Western author), 1 Western.

### Mathematical Modeling of Catalytic Gas-Phase Polymerization of Ethylene in Fluidized Bed

937M0082C Kiev *KHIMICHESKAYA TEKHNLOGIYA* in Russian No 2, Mar-Apr 92 pp 71-76

[Article by V. N. Orlik, Yu. V. Kolesnik, Yu. I. Goglyuvatyy; UDC 66.096.5.001.572]

[Abstract] Mathematical description of a fluidized bed is made difficult by the complex hydrodynamic situation in the bed, with chaotic development, growth and passage of bubbles through the bed, nonuniform distribution of gas and particle velocities through the cross section of the reactor, large-scale particle circulation, etc. This article presents a mathematical model of the processing of gas-phase polymerization of ethylene in a fluidized catalyst bed based on a two-phase fluidization theory, assuming that the bubble phase is in a quasi steady ideal extraction mode, the bubbles are spherical, growing through the height of the bed, polymerization does not occur in the gas bubbles, while the solid phase is in an ideal mixing mode, with the quantity of gas necessary for fluidization. The particles are assumed to be small, heat and mass transfer between emulsion and

bubble phases occurring with identical intensity throughout the height of the bed, catalyst feed is constant, separation of solid particles and deactivation of catalysts are ignored, the product is removed at a rate which maintains constant bed height. Figures 3; References 2: 1 Russian, 1 Western.

### Effectiveness of Thermocatalytic Industrial Stack Gas Purification System

937M0082F Kiev *KHIMICHESKAYA TEKHNLOGIYA* in Russian No 2, Mar-Apr 92 pp 91-95

[Article by G. N. Lyubchik, V. A. Khristich, L. V. Ivannikova, M. Zembzhuski, R. Miller, T. Banashak; UDC 632.15]

[Abstract] A typical thermocatalytic stack gas purification unit consists of a heat recovery element, additional flame stack gas heater and a catalytic element. The additional flame heater maintains the proper temperature conditions and largely determines the energy efficiency and ecological effectiveness of the system. Therefore, problems of coordinating the operating mode of the component elements of the system must be given great attention during the design as well as operation of the system. Equations are presented for computation of the operational characteristics of such a purification system. The degree of heat recovery and impurity concentration are found to have a great influence on the energy efficiency and ecological effectiveness of the system. Figures 2; References 5: Russian.

### THEORETICAL PRINCIPLES OF CATALYTIC STACK GAS PURIFICATION PROCESSES

937M0082G Kiev *KHIMICHESKAYA TEKHNLOGIYA* in Russian No 2, Mar-Apr 92 pp 95-98

[Article by V. A. Makarenko, V. Ye. Kundos, K. S. Los, V. V. Chilovskiy; UDC 628.539:66.011]

[Abstract] The authors have undertaken a system of experimental and theoretical studies to determine the scientific bases for development and design of catalytic stack gas purification systems intended to remove  $NO_x$ , CO and hydrocarbons. Thermodynamic analysis has determined the area of optimal conditions for conducting catalytic purification of combustion products to remove oxides of nitrogen and other toxic components. The promise of multistage removal of various harmful substances in reducing and oxidizing media has been demonstrated. Laboratory studies have been performed on the kinetics of catalytic conversions. The area of application of thermodynamic analysis is expanded by

the fact that the basic combustion products are in a near-equilibrium state in typical stack gas, allowing the analysis to be used to process the results of kinetic experiments. Engineering methods for designing fuel combustion devices and thermocatalytic reactors with catalytic reduction of oxides of nitrogen have been developed. The Institute of Gas, Ukrainian Academy of Sciences, has developed a design for a gas-air heat generator and suggested a boiler design with catalytic purification of combustion products. Figure 1; References 6; Russian.

#### **Stereoselective Hydrogenation of N-Alkynes on Boron-Nickel Catalysts**

937M0084B Ivanovo IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: KHIMIYA IKHIMICHESKAYA TEKHNLOGIYA in Russian Vol 47 No 6, Jun 92 pp 76-80

[Article by S. S. Petrova, E. Kh. Siymer, I. I. Amitan; UDC 66.096.12:547.314]

[Abstract] Stereoselective hydrogenation of higher alkynes with inner placement of the triple bond has been little studied. This article is intended to aid in the selection and determination of the composition of catalysts for stereoselective synthesis of cis-alkenes. Nickel semiboride ( $\text{Ni}_2\text{B}$ ) and trinickel boride ( $\text{Ni}_3\text{B}$ ) were tested as well as a modified boron-nickel catalyst ( $\text{NiB}$ ) described earlier. The boron content was 80, 60 and 20% in the three catalysts. Hydrogenation was performed in a thermostated boat with an agitator. Products were analyzed by capillary GLC on 1,2,3-tris-(2-cyanoethoxy) propane. The  $\text{NiB}$  catalyst is recommended, modified with 2-phenol-1,5-dimethylpyrazol-2-one. This catalyst is effective at 15° C, atmospheric pressure of hydrogen, has high activity and stereoselectivity. Hydrogenation on  $\text{NiB}$  is also not complicated by secondary reactions such as destruction and polymerization. Figure 1; References 7; 6 Russian, 1 Western.

#### **Mixed-Ligand Binuclear Complex of Copper (II) With Glycinate and $\text{EDTA}^{4-}$ -Ions—Catalyst for Oxidation of Sodium Sulfide With Molecular Oxidation**

937M0087C Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 8, Aug 92 pp 1798-1801

[Article by A. P. Gerbeleu; UDC (541.49+546:562+546.221):541.128]

[Abstract] Results are presented from a study of the oxidation of sodium sulfide with molecular oxygen using a mixed-ligand copper (II) complex with the composition  $(\text{DuGl})_2\text{EDTA}(\text{I})$  as the catalyst in the presence of a double excess of glycine which facilitates maintenance of catalyst solution homogeneity at pH10. The  $\text{EDTA}^{4-}$  ion acts as the center of the complex molecule, with each of the two iminodiacetate groups bonded to one copper ion. Kinetic measurements were performed by a gasometric

method under static conditions. An intermediate product is formed which is the result of interaction of sodium sulfide with complex I and contains no oxygen. The formation of the intermediate indicates that the chemical reaction of oxidation occurs on the surface of the  $\text{S}^{2-}$  and is a heterogeneous catalytic process. Figures 4; References 9; 8 Russian, 1 Western.

#### **Catalase Activity of Copper (II) Hydroxocomplexes With Salicylate Ion**

937M0087D Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 8, Aug 92 pp 1830-1836

[Article by A. P. Gerbeleu; UDC 541.49+541.128.12]

[Abstract] Mono-, bi- or polynuclear transition metal complexes can simulate the action of catalase in model reactions. This article studies the "catalase" activity of copper (II) complexes with the salicylate ion. It is found that a 1:4 copper:salicylate solution at  $\text{pH} > 9$  has high catalytic activity in decomposition of  $\text{H}_2\text{O}_2$ . The maximum reaction rate is seen at pH 10.4. The maximum reaction rate is achieved with virtually equimolar content of both hydroxocomplexes, indicating that in the presence of hydrogen peroxide they interact to form a binuclear peroxocomplex. The catalytic effect of the copper complexes increases the reaction rate by more than a factor of four, indicating great catalytic activity than that of the previously studied mixed-ligand binuclear complex of copper (II) with glycinate and ethylene diamine tetraacetate ions. Figures 4; References 10; 4 Russian, 6 Western.

#### **Intensification of Catalytic Action of Copper (II) Chloride on Solution Process of Copper in Presence of Iron (III) Ions**

937M0115A St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 3, Mar 92 (manuscript received 20 Jun 91) pp 552-556

[Article by E. B. Khobotova, O. T. Nikolov, Yu. V. Kholin, S. D. Gorobets, Scientific Research Institute of Chemistry, Kharkov State University; UDC 546.56:541.128.12]

[Abstract] The goal of this work was to try to explain the reasons for increased rate of copper solution in concentrated copper-iron chloride solutions with a given copper:iron ratio. The relationship of this effect to the ability to form heteronuclear complexes  $\text{Cu}(\text{II})\text{-Fe}(\text{III})$  was investigated in similar systems. EPR spectra made it possible to observe complex formation of paramagnetic particles and the degree of the localization of unpaired electron on the central atom. Analysis of EPR spectra showed that heteronuclear complexes  $\text{CuFeCl}_3$  containing  $\text{Cl}^-$  ions in their composition did form in hydrochloric solutions. Due to a transfer of electronic charge from the  $\text{Fe}(\text{III})$  ion ligand to  $\text{Cu}(\text{II})$  ion, the effective charge on copper diminished. This process evidently

results in increased catalytic activity of copper compounds. The stability constant of this complex was determined. An increase in the solution rate of copper was noted in complex rich solutions. Table 1; figures 4; references 16: 13 Russian, 3 Western (1 by Russian authors).

**Relationship Between Acid and Oxidation-Reduction Properties of Mixed Yttrium-Cerium Silicates and Their Catalytic Properties in Oxidation of Carbon (II) Oxide**

937M0115C St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65, No 3, Mar 92 (manuscript received 25 Oct 91) pp 625-628

[Article by G. V. Larina, G. K. Ragulin, A. S. Turbin, V. N. Pak, Russian State Pedagogical University imeni A. I. Gertsen; UDC 541.183.02:546..98]

[Abstract] In this paper attention was directed to the consistent changes in acidic, reduction-oxidation and catalytic properties of mixed amorphous yttrium-cerium silicates related to the Y/Ce molar ratio in the composition of the materials examined. Observed similarities in the functions obtained point out possible commonality in the causes for this phenomenon, most probably related to the mutually interactive effect of rare earth elements in these systems. Adsorption studies showed that the synthesized silicates have finely porous structures and well developed surface, stable even during calcination at 500°. It was shown that the surface activity of Y,Ce-silicates, which reaches a maximum with an 80% content of cerium, is primarily due to the Lewis type acid centers. Most probably they are related to coordination unsaturation and the electron accepting ability of the

surface Ce(IV) ions. Catalytic oxidation of carbon (II) oxide on Y,Ce- silicate was performed showing that the catalyst was only moderately active; only above 300° was a marked oxidation of CO noted. It appeared that Lewis acidity and the oxidative ability of the surface of Ce-silicates are interrelated and act in closely coordinated way in the catalytic processes. Table 1; references 10: 9 Russian (1 by Western author), 1 Western.

**Effect of Extraction Process on Catalytic Oxidation of Hydrazine With Nitric Acid in Presence of Actinoid Elements**

937M0122B St. Petersburg RADIOKHIMIYA in Russian Vol 34, No 4, Jul-Aug 92 pp 34-41

[Article by B. Ya. Zilberman, A. N. Mashkin; UDC 546.171.5:546.171.8:546.79:66.061.5]

[Abstract] The goal of this work was to investigate the effect of the extraction process and addition of uranium, plutonium and neptunium on oxidation of hydrazine. special attention was paid to the reaction of hydrazine with nitric acid in single and dual phase systems. In the single phase system uranium and neptunium show little effect on the rate of hydrazine breakdown; after the termination of the rapid stage the process is practically stopped. In the presence of plutonium the process runs slower but much more completely. In the dual phase system the process is also more complete than in the single phase and the actinoid elements appear to accelerate it. The effect of plutonium is significant only at a Pu/Tc ratio of less than 0.2; further increase of Pu has no practical effect on the kinetic curve. After decomposition of hydrazine in the dual process, its breakdown rate is markedly increased. Figures 6; references: 4 (Russian).

**Complexing and Hydrolysis as Competing Processes in Water-Salt Systems**

937M0088A Moscow KOORDINATSIONNAYA  
KHIMIYA in Russian Vol 18, No 8 Aug 92  
(manuscript received 24 Feb 92) pp 803-807

[Article by G. V. Kozhevnikova; Petersburg State University; UDC 542.938:541.65:535.343]

[Abstract] Studies of solutions of some salts containing hydrolyzing 2-charge cations ( $Zn^{2+}$ ,  $Cd^{2+}$ ,

$Hg^{2+}$ ), and 3-charge cations ( $Al^{3+}$ ,  $Ga^{3+}$ ,  $In^{3+}$ ,  $Bi^{3+}$ ) and anions of strong acids ( $NO_3^-$ ,  $Cl^-$ ) were performed by combination scattering spectroscopy. The influence of acidity on complexing and the nature of the ligands on hydrolysis were studied. Spectroscopy demonstrated the dependence of complexing processes on the acidity of the solutions and on the hydrolytic capacity of the cations. The dependence of complexing processes on hydrolysis was demonstrated. Figures 3; references 11: 6 Russian; 5 Western.



### Laws of Ignition in the System Carborane-4 + Water Vapor

937M0142A Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 12, Dec 92 (manuscript received  
30 Apr 92) pp 1640-1642

[Article by Ye.V. Bepalov, O.D. Kazakov, Ye.S. Severin, and V.G. Slutskiy, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 541.124]

[Abstract] The formation kinetics of a condensed phase in carborane-argon and carborane-water vapor-argon systems was studied at temperatures of 920 to 1,020 K under a pressure of 0.1 MPa. The first of the two study systems contained  $0.01\text{C}_2\text{B}_4\text{H}_6 + \text{Ar}$ . The second system contained 12% water vapor, i.e., it consisted of  $0.01\text{C}_2\text{B}_4\text{H}_6 + 0.12\text{H}_2\text{O} + \text{Ar}$ . Each of the gas mixtures was premixed in a 1,250-cm<sup>3</sup> mixer heated to 360 K and then passed into an evacuated cylindrical quartz sample cell. The passage process lasted about 0.05 seconds, and the measurements took from 0.3 to 3 seconds. The light absorption at different wavelengths ( $\lambda = 270$  to 500 nm) as the gas mixtures passed through the sample cells was measured. The studies established that the carborane pyrolysis products undergo oxidation by the water vapor, whereas the carborane itself does not react with the water vapors. A comparison of the time characteristics of carborane pyrolysis and ignition in the system carborane + water vapor at temperatures of 900 to 1,600 K revealed that at temperatures above 1,000 K, ignition occurs in the stage of carborane pyrolysis. At temperatures below 1,000 K, on the other hand, ignition occurs after pyrolysis of the carborane has been completed. Figures 2; references 5 (Russian).

### The Ignition of Chemically Active Media in Closed Spaces by Charged Particles

937M0142B Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 12, Dec 92 (manuscript received  
27 Jan 92) pp 1643-1648

[Article by S.A. Kazarin; UDC 536.46]

[Abstract] The dynamics of the ignition of chemically active media in closed shells by a flow of heavy charged particles (protons) was examined in a numerical study. The analysis included consideration for the multistage nature of the chemical reactions and pressure as a function of flow intensity. Specifically, it was assumed that a chemically active medium with a thickness of  $l_1$  is located in a closed space formed by walls of finite thickness that are directly adjacent to the chemically active medium without any gas interlayer. The heating of the chemically active medium due to conversion of the beam energy into thermal energy, heat conducted from the heated wall, and radiolysis (direct decomposition of the chemically active medium under the effect of the flow of particles) results in either melting or gasification of the material. It was further assumed that phase transition processes involving both absorption and heat release may occur. The gaseous products formed as a result of the first reaction

were assumed to participate in two subsequent reactions leading to the formation of the final components, and the radiolysis products were assumed to not participate in any further chemical reactions. The appearance of gaseous components was assumed to be accompanied by an increase in pressure in the closed space that quickly equalized throughout the space. The following assumptions were also made: The condensed phase is incompressible, all reactions follow Arrhenius' law, the reaction products are subordinate to van der Waals' law, and mutual diffusion of the reaction components occurs in the reaction products. Finally, it was assumed that the wall bounding the closed space is not deformed regardless of the pressure or temperature and that the bulk energy absorption, the thermal effects of the chemical reactions and radiolysis, and radiation losses by the heated walls were the energy sources and drains. The mathematical analysis performed established that as the irradiation intensity is decreased, the energy expenditures required for ignitions increase. Dependences of the ignition parameters on particle beam intensity for fixed enclosure thicknesses and particle energies were derived. Figures 3; references 6 (Russian).

### A Numerical Model of Heterogeneous Combustion in a Porous Medium

937M0142C Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 12, Dec 92 (manuscript received  
19 Feb 92) pp 1649-1654

[Article by Ye.M. Tonkopi, G.B. Manelis, and S.V. Kulikov; UDC 536.46]

[Abstract] A mathematical model of filtration combustion has been proposed that makes it possible to give more detailed consideration to the kinetics of chemical transformations. The model includes equations describing the transfer of each of the reacting components and heat transfer, as well as an equation of the state of the gas. The problem of heterogeneous combustion in a porous medium is reduced to the solution of a system of differential equations relative to the temperature and concentrations of component, and the unknown velocity of the front is the eigenvalue of a stationary problem. The equations constituting the model were integrated numerically in accordance with a special implicitly finite-difference scheme by using ranging methods. The results of test calculations (for one coal combustion reaction, i.e.,  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ ) made by using the proposed model with simplified kinetics were found to be consistent with data from laboratory experiments. Calculations were also performed for eight multicomponent systems with consideration for their more complex kinetics. The effect of external heat losses was also studied. The study demonstrated that as the coefficient of heat loss increases, the velocity of the front, velocity of the blast of oxidizing agent required for a mode of complete transformation, and combustion temperature

accompanying such a mode all increase. Figures 3; references 9: 5 Russian, 4 Western.

### **The Thermal Instability of Nonadiabatic Flame Propagation in a Flow of Condensed Mixture**

937M0142D Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 12, Dec 92 (manuscript received  
18 Dec 92) pp 1655-1664

[Article by A.I. Mamedov, P.M. Krishenik, G.B. Manelis, N.K. Nadirov, S.I. Khudyayev, and G.V. Shkadinskaya, Chemical Physics Institute, Russian Academy of Sciences, Chernogolovka, and Structural Macrokinetics Institute, Russian Academy of Sciences, Chernogolovka; UDC 536.36]

[Abstract] The effect of heat losses on the stability of combustion in a flow of condensed mixture was examined within the framework of a perturbation theory. The theoretical examination was based on the method of asymptotic expansions in terms of a perturbation designating the width of the combustion zone. Unlike previous analyses, this analysis gave consideration to effect that heat loss to the side walls has on the stability of a combustion wave with respect to one-dimensional disturbances. A semi-infinite plug-flow tube reactor with external heat exchange within which an exothermal reaction occurs was considered in the analysis. It was assumed that the condensed or liquid-phase reagents enter the combustion zone through the cooled reactor inlet. The boundaries of fluctuating and monotonic instability were found in the parametric range of the problem. The mathematical analysis performed established that as lateral heat losses increase, the zone of unstable (pulsating) combustion expands. The boundaries of fluctuating instability in the parametric regions were found to have an extremum associated with the existence of both lateral heat losses and heat losses at the reactor's end. A numerical analysis of the nonstationary problem confirmed the conclusions of the approximate analysis performed by using asymptotic expansions based on the perturbation method. Nonstationary phenomena thus have a significant effect on the nature of the wave process of transformation in the flow and must therefore be given detailed consideration when conducting experiments and developing new technological processes. Figures 2; references 30: 21 Russian, 9 Western.

### **The Spontaneous Combustion of a Gas Mixture Before the Flame Front Given Different Intensities of Turbulence in the Combustion Chamber**

937M0142E Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 12, Dec 92 (manuscript received  
16 Dec 91) pp 1665-1676

[Article by A.N. Lipatnikov, Moscow Physics Technology Institute; UDC 621.434]

[Abstract] A numerical model is presented that is intended for use in studying the effect of turbulence on the spontaneous combustion of a premixed mixture under conditions

simulating spark engines. As in other engineering models of the processes occurring in the combustion chambers of internal combustion engines, the proposed model describes combustion in terms of one variable, i.e., the degree of the development of the combustion products' reaction ( $Y$ ). The popular BML method is used to average the rate of change in  $Y$ , the  $k$ - $\epsilon$  model is used to describe the evolution of the turbulence parameters, and the Shell model is used to describe the preignition processes. The analysis performed demonstrated that intensification of turbulence (i.e., an increase in pulsation velocity) suppresses spontaneous combustion by accelerating the flame front. Turbulent diffusion was found to accelerate inflammation, whereas turbulent heat transfer had the opposite effect and proved to be less significant. The analysis further established that turbulent diffusion (i.e., turbulent reagent transfer) may initiate spontaneous combustion when a cold flame arises in the adjacent zone with a lower temperature. According to the calculations performed on the basis of the proposed model, a drop in heat removal may retard spontaneous combustion, although the delay in inflammation decreases as the initial temperature increases. Figures 5, table 1; references 17: 10 Russian, 7 Western.

### **Optimizing the Surface Heat Treatment of Polymeric Materials To Reduce Their Combustibility**

937M0142F Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 12, Dec 92 (manuscript received  
16 Mar 92) pp 1677-1682

[Article by S.Ye. Selivanov and A.A. Shiyan, Kharkov Construction Engineering Institute; UDC 536.4:541.124:691.175]

[Abstract] Research on the problem of reducing the combustibility of polymeric materials has established that preliminary heat treatment of a polymeric material's surface is one promising way of reducing combustibility. Specifically, experiments have established that a surface layer 50 to 200  $\mu\text{m}$  thick limits the processes responsible for ignition and flame propagation throughout a polymer. Combined heating and laser irradiation of the surfaces of polymeric materials have proved to be especially promising. Research has also revealed a broad spectrum of factors leading to fluctuations in the thermodynamic parameters of polymeric materials during the course of their modification. Such fluctuations (which may be looked upon as noise) lead to variations in the degree of cross-linking of a polymer's macromolecules and in a decrease in the most likely degree of cross-linking. In the case of filled polymers, the filler may have a significant effect on the properties of the given polymeric material during modification (heat treatment). It thus follows that individuals designing process trains for the surface modification of polymeric materials work to eliminate the very diverse fluctuations that can occur during the modification process. If these fluctuations cannot be eliminated, the presence of scattering in the value found for the degree of cross-linking must be taken into account when using the given modified polymeric material. Figures 3; references 7 (Russian).

### NEW ELECTROCHEMICAL REACTIONS AND MEMBRANE MATERIALS IN IONOMETRY

937M0083A Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 47 No 8, Aug 92 pp 1349-1357

[Article by O. M. Petrukhin; UDC 543.257.1]

[Abstract] Attention is drawn to new membrane materials and studies in areas of ionometry with great growth potential. Examples are presented of new and unusual electrode-active compounds, including phosphate glasses containing no alkali metals and organotin compounds with the hydrophosphate ion. Heterogeneous reactions of macrocyclic ionophors are quite promising in organic analysis in terms of the possible width of their area of utilization, particularly in the determination of stereo isomers. The problem of creating membrane phases in the manufacture of ion-selective field-effect transistors can be solved by the use of Langmuir-Blodgett films. Figure 1; References 31: 14 Russian, 17 Western.

### Influence of Thermal Modification and Properties of Carrier on Characteristics of Gas Chromatographic Sorbents Based on Polyethylene Glycols

937M0083B Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 47 No 8, Aug 92 pp 1442-1447

[Article by S. A. Volkov, V. Yu. Zelvenskiy, G. A. Smolyaninov; UDC 543.544]

[Abstract] A comparison is presented of the basic characteristics of thermal polyethylene glycol sorbents and sorbents based on the same immobile liquid phases and solid carriers but subjected to conditioning at temperatures not exceeding the maximum operating temperature of the immobile liquid phases. The change in properties of the polyethylene glycol as a function of type of carrier used is also discussed. Thermal modification of the polyethylene glycol-based sorbent with diatomite carrier is found to increase the degree of chromatographic separation of polar compounds. A thermally modified sorbent based on tsvetokhrom C and polyethylene glycol 20,000 is found to have the best chromatographic properties. Figures 2; References 13: 6 Russian, 7 Western.

### Nitrate-Selective Electrodes Based on Complexes of Metals With Phosphorylated Azapodands

937M0083C Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 47 No 8, Aug 92 pp 1448-1450

[Article by A. R. Garifzyanov, Ye. Yu. Mikryukova, I. I. Musyna, V. F. Toropova; UDC 543.343:621.2.035.2]

[Abstract] This work studies the electrode properties of complexes of copper, palladium and mercury with phosphorylated azapodands. The ion-selective electrodes

developed, based on metal complexes with phosphorylated azapodand, can be used to determine  $\text{NO}_3^-$  in food products. The electrodes are highly stable over a broad pH range and over extended time. The calibration characteristic is linear at  $1 \cdot 10^{-1} - 1 \cdot 10^{-5} \text{ mol/l NO}_3^-$ . A 30-100 times excess of  $\text{H}_2\text{PO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  does not hinder the determination. References 3: Russian.

### Electrochemical Properties and Analytic Capabilities of Film Electrodes Selective for Nonionogenic Surfactants

937M0083D Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 47 No 8, Aug 92 pp 1464-1471

[Article by R. K. Chernova, Ye. G. Kulapina, Ye. A. Materova, Ye. V. Tretyachenko, A. P. Novykov; UDC 543.257.1:661.185.1]

[Abstract] This work studies the influence of the number of oxyethyl groups and the length of the hydrocarbon radical on the electrochemical properties and analytic capabilities of selective film nonionogenic surfactant electrodes based on  $\text{AP}_m\text{-n-Ba}$ -tetraphenyl borate where  $\text{AP}_m\text{-n}$ -oxyethylated alkylphenols  $\text{C}_m\text{H}_{2m+1}\text{C}_6\text{H}_4\text{O}(\text{C}_2\text{H}_4)_n\text{nf}_4$  with  $n=3-100$  and  $m=8-12$ . The conductivity of membranes of various compositions was measured and radioactive  $^{85}\text{Sr}$  was used to study processes at the membrane-solution interface. The possibility is demonstrated of separate determination of alkylphenols in some binary mixtures. Metal ions are transferred to the membrane-solution interface and ions are transported in the membranes. Figures 4; References 14: 7 Russian, 7 Western.

### Electrochemical Reduction of Phosphates Containing Fluorinated Radicals

937M0120E St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 62 No 5, May 92 (manuscript  
received 10 Oct 91) pp 1099-1103

[Article by G. K. Budnikov, O. Yu. Mironova, V. V. Yanilkin, Kazan State University imeni V. I. Ulyanov-Lenin; UDC 541.138.3:547.558.1]

[Abstract] Derivatives of pentavalent, tetra-coordinated phosphorus containing fluorinated fragments possess interesting biological properties. There are practically no data reported on electrochemical behavior of such compounds. In this work, electrochemical reduction of cyclic and acyclic fluorine containing derivatives of phosphoric and phosphonic acids were investigated in hope of finding an analytical signal for such compounds and identifying factors affecting its size. Fluorinated aryl, salicyl- and alkylphosphates were investigated with classical polarography, cyclic volt-amperometry, preparative electrolysis and EPR spectrometry. Analysis of polarographic curves led to possible mechanisms involved in these reductions. Table 1; figure 1; references 13: 12 Russian (1 by Western authors), 1 Western.

### Solid Electrolytes in Sensor Technology

937M0134B Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 10, Oct 92 (manuscript received 7 Apr 92) pp  
1444-1449

[Article by Ya. Ya. Kleperis, G. E. Bayars, G. Ya. Vayvars, A. A. Kranevskis, A. R. Lasis, Institute of Solid State Physics, Latvian University, Riga; UDC 543.272.2.082+541.133]

[Abstract] The goal of this work was to investigate the effect of the production technology of solid film and ceramic electrolytes (solid gel of antimony acid hydrate and ceramic ammonium  $\beta$ -alumina), that of the working electrode and measurement conditions on the sensitivity and selectivity towards various gasses. Analysis of experimental results obtained on the change of the resistance of the ceramic  $\beta$ -alumina samples showed that their sensitivity to ammonia is a function of the method of the preparation of test samples. Selectivity of  $\beta$ -alumina to various gasses may be altered by selection of the corresponding electrode and its polarization. The solid gel of the antimony acid hydrate film proved to be the proper solid electrolyte for the production of gas sensors whose selectivity could be varied by changing the electrode material or the procedure used in measurements and by doping the gel film. Figures 5; references 11: 1 Russian, 10 Western (2 by Russian authors).

### Electrochromic Mirrors - Solid Ionic Devices

937M0134C Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 10, Oct 92 (manuscript received 3 Apr 92) pp  
1450-1455

[Article by Ya. Ya. Kleperis, A. N. Rodionov, A. R. Lasis, Institute of Solid State Physics, Latvian University, Riga; UDC 539.234/213:535.33/34]

[Abstract] Optical and electrochemical properties of solid state thin film electrochromic devices controlled by their coefficient of reflection were investigated. The following systems were prepared for this work: 1) functionally unified devices: ITO/ $\text{WO}_3/\text{SiO}_x/\text{Au}$ ; ITO/ $\text{IrO}_x/\text{SiO}_x/\text{WO}_3/\text{Al}$  and  $\text{WO}_3/\text{Pd}/\text{SiO}_x/\text{WO}_3/\text{Au}$ , as well as 2) functionally separated device: ITO/ $\text{WO}_3/\text{Pd}/\text{SiO}_x/\text{WO}_3/\text{Au}$ . Electrochromic mirrors, whose reflection is controlled by diffusion, exhibited the greatest reduction of the white light; the common electrochromic system showed maximum values of the reflection modulation. Kinetic curves and reflection spectra of the test mirrors were presented. Overall, the results showed that these materials could be used effectively in production of mirrors with controllable reflection coefficients. The optical parameters were better in systems with minimal layers preceding the reflector film but the current characteristics were better in case of the complementary and the commonly used electrochromic systems. Table 1; figures 6; references 9: 4 Russian (1 by Western author) 5 Western (2 by Russian authors).

### Solid Electrolytes in $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ System Based on Tetragonal Solid Solutions

937M0134E Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 10, Oct 92 (manuscript received 2 Apr 92) pp  
1484-1489

[Article by Yu. N. Karavayev, Ye. I. Burmakin, Institute of Electrochemistry, Ural Division, Russian Academy of Sciences, Yekaterinburg; UDC 541.135-165:548.1.022]

[Abstract] Electric conductivity of solid solutions in the system  $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$  was investigated in temperature range 400-1100° C. It was shown that addition of cerium oxide stabilized the monophasic structure of tetragonal and fluorite-like solid solutions whose electric conductivity at temperatures below 400° C was similar. After repeated tests at that temperature all samples with either of the two structures retained their initial values of the electric conductivity. The oxygen concentration showed no effect on it, indicating that their conductivity was almost purely ionic in a wide range of the partial oxygen pressures. Because of this characteristic they could be used as solid electrolytes in electrochemical devices such as oxygen sensors. Tables 2; figures 3; references 7: 2 Russian, 5 Western.

### Electric Properties of Solid Electrolytes With General Formula $(\text{GeS})_{1-x}(\text{AgAsS}_2)_x$

937M0134G Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 10, Oct 92 (manuscript received 23 Mar 92)  
pp 1523-1530

[Article by V. B. Zlokazov, N. V. Melnikova, Ye. R. Baranova, M. V. Perfilyev, L. Ya. Kobelev, Ural State University, Yekaterinburg; UDC 537.311.322]

[Abstract] The goal of this work was to investigate some electric properties (impedance and electric conductivity along with dielectric permeability as functions of the temperature) of the materials synthesized in the system  $(\text{GeS})_{1-x}(\text{AgAsS}_2)_x$  where  $x = 0.1; 0.2; 0.3; 0.5$ ; and 0.9, and of the compound  $\text{CuGeAsS}_3$  in the temperature range 78-500 K and frequencies ranging from  $10^{-2}$  to  $10^5$ . One could assume that, since the monovalent copper ions resemble silver ions, copper ions mobility could be expected in  $\text{CuGeAsS}_3$  analogously to the situation observed with copper chalcogenides and halides ( $\text{Cu}_2\text{S}$ ,  $\text{CuI}$ ,  $\text{CuBr}$ ). Ionic conductivity was observed along the silver ions in these compounds. At 300 K and  $x = 0.5$  this conductivity reached almost 100%. On the basis of an analysis of the impedance and admittance of these materials, frequency ranges were found in which the electrode processes had no effect on electric measurements. It was concluded that these materials could find application in micro- and optical electronics. Tables 3; figures 5; references 12: 11 Russian, 1 Western (by Russian authors).



**Oxygen Chemosorption by Oxide Electrodes Based on  $\text{SnO}_2$  in Solid Electrolytes**

937M0134H Moscow ELEKTROKHIMIYA in Russian Vol 28 No 10, Oct 92 (manuscript received 24 Apr 92) pp 1567-1575

[Article by Yu. A. Dobrovolskiy, G. V. Kalinnikov, Institute of Novel Chemical Problems, Russian Academy of Sciences, Chernogolovka; UDC 541.135]

[Abstract] Semiconducting oxide materials are widely used in sensitive elements of gas sensors. The goal of this work was to investigate chemical sorption of oxygen on doped tin dioxide ( $\text{SnO}_2\text{-V}_2\text{O}_5/\text{Na}_3\text{GdSi}_4\text{O}_{12}$ ) by identifying regions of the existence of various oxygen forms on borders of the dual phase  $\text{SnO}_2$ /gas system and a ternary phase system  $\text{SnO}_2$ /solid electrolyte/gas in relationship to the temperature and vanadium oxide concentration in the semiconductor. On the basis of thermal desorption spectra, three adsorption forms of oxygen were identified on the surface of the semiconductor: a physically adsorbed molecularly unchanged form, a molecular-radical form and an atomic-ionized form. The parameters of the formation processes and of the breakdown of these three forms were calculated. Their relationship to the concentration of the doping component was determined. It was established that during the contact of solid electrolyte with semiconductor oxides, the atomic-ionized oxygen was not desorbed from the surface but became a component of the solid electrolyte. Existence of this equilibrium between the oxygen of tin dioxide lattice and the surface oxygen can lead to an  $\text{O}^{2-}$  ion exchange between solid electrolyte and the semiconductor lattice. Tables 3; figures 7; references 14: 7 Russian (1 by Western authors), 7 Western (2 by Russian authors).

**Electric Conductivity in  $\text{CaH}_2\text{-LiH}$  and  $\text{CaH}_2\text{-CaF}_2$  Systems**

937M0134I Moscow ELEKTROKHIMIYA in Russian Vol 28 No 10, Oct 92 (manuscript received 31 Mar 91) pp 1578-1580

[Article by V. P. Gorelov, S. F. Palguyev, Institute of Electrochemistry, Ural Division, Russian Academy of Sciences, Yekaterinburg; UDC 541.133.08]

[Abstract] Calcium hydrate undergoes phase transition at about 1053 K at which the low temperature orthorhombic structure converts to a cubic, fluoride type structure. This new structure favors anionic conductivity and the goal of this work was to determine whether it

would be possible to stabilize the high conductivity, high temperature form of calcium hydride with LiH and  $\text{CaF}_2$  additives and to study the effect of these additives on electric conductivity of calcium hydride. It was noted that addition of LiH to calcium hydride increased the electric conductivity; with temperature increase to 863 K a jump-like decrease in the resistance was noted, which was ascribed to the melting of the eutectics based on LiH. Addition of LiH did not seem to stabilize the cubic form of calcium hydride. Addition of  $\text{CaF}_2$  to  $\text{CaH}_2$  lowered the temperature of polymorphic conversions in the latter; with increased concentration of  $\text{CaF}_2$  electric conductivity of the low temperature phase increased and that of the high temperature, cubic phase - decreased. It was noted that the defective structure of solid solutions  $\text{CaH}_2\text{-CaF}_2$  is primarily the result of oxygen admixtures and therefore it was concluded that the ionic transfer must have occurred by the vacancy mechanism. Figures 2; references 9: 4 Russian, 5 Western.

**Synthesis of Sulfur Containing Structural Analogs of Group K Vitamins by Electrochemical Method**

937M0137B Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 11, Nov 92 (manuscript received 12 Dec 91) pp 2605-2608

[Article by M. Ye. Niyazymbetov, I. V. Arefyeva, Ye. I. Zakharova, L. D. Konyushkin, S. M. Alekseyev, V. P. Litvinov, R. P. Yevstigneyeva, Institute of Organic Chemistry imeni N. D. Zelinskiy, Russian Academy of Sciences, Moscow; Institute of Fine Chemical Technology imeni M. V. Lomonosov, Moscow; UDC 541.138:547.655\*27]

[Abstract] Thio-ethers of 2-methyl-1,4-naphthoquinone (2MNQ), structural analogs of group K vitamins, exhibit marked anti-hemorrhagic activity; analogous derivatives show also antibacterial, fungicidal and anti-tuberculin activity. An effective electrochemical synthetic method was reported for 3-alkylthio- and 3-acylthioethers of 2MNQ. Equimolar quantities of 2MNQ and mercaptan in 0.02-0.03 N solution of  $\text{Et}_4\text{NBr}$  in MeCN are placed in the cathode compartment of the electrolyzer and electrolyzed with stirring at 20° using a platinum cathode. After completion of this process, air is bubbled through for one hour, the products are separated by filtering or by extraction and purified on a chromatographic column. Without passing electricity through the reaction medium no reaction was observed to take place. Tables 2; references 12: 5 Russian, 7 Western.



**Biological Purification of Effluent From Petrochemical Production**

937M0074B Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 14 No 3, Mar 92 (manuscript received 1 Aug 91) pp 221-225

[Article by A. M. Petrov, O. I. Yakusheva, R. P. Naumova, Kazan State University imeni V. I. Ulyanov-Lenin; Production Association "Nizhnekamskneftekhim", Nizhnekamsk; UDC 628.35]

[Abstract] During the production process of styrene and propylene oxide (SPO) by dehydration of methylphenyl carbinol, effluent is formed containing phenol, acetophenone, styrene, glycols and other organic impurities. The goal of this work was to investigate the potential of local aerobic purification of such effluent using immobilized microorganisms. Model experiments in a system consisting of four sequentially connected biotanks showed that it was possible to remove 95-97% of organic pollutants whose initial concentration was 5.2 g/l of COD. A 2-month purification course of industrial effluent by this method gave a 0.26 g/l COD level with some opalescence of the water but no color or odor in the final samples. Purification of actual industrial effluent is being performed and the decisive role in this process is being ascribed to gram-negative bacteria, especially the SPI whose fraction in successfully operating biotanks increased from 21 to 95%. Table 1; figures 4; references 10: 4 Russian, 6 Western.

**Photometric Determination of Microquantities of Aluminum in Drinking Water**

937M0076C Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 58 No 2, Feb 92 (manuscript received 4 Mar 91) pp 183-187

[Article by L. I. Savranskiy, O. Yu. Nadzhafova, Kiev University; UDC 543.43:543.421:546.621]

[Abstract] Determination of aluminum in water is an important method of analytical control of this element. In order to improve chemical analytical characteristics of the reaction of aluminum with chromazurol S (which normally is used in determination of its microquantities) the reaction was studied in the presence of cetyl pyridinium chloride (CP) and of hydroxyethyl ether of alkylphenols (cationic and non-ionic surfactants, respectively). Analysis of the results obtained on model runs and actual analysis of tap water showed that this approach removed the competing effect of excess CP, allowed expansion of the range of optimal acidity and increased the sensitivity of this method. Effect of iron (III) and copper (II) was eliminated by addition of hydroxylamine hydrochloride and 1,10-phenantroline. The mixture of the necessary reagents was stable for up to two weeks when stored at cold temperature in darkness. The method was recommended for testing for trace quantities of aluminum in tap water. Tables 3; figure 1; references 12: 10 Russian, 2 Western.

**Purification of Industrial Wastewater To Remove Mercury**

937M0082A Kiev *KHIMICHESKAYA TEKHOLOGIYA* in Russian No 2, Mar-Apr 92 pp 15-18

[Article by L. Ye. Postolov, T. Ye. Mitchenko, V. G. Ovchinnikov, V. V. Trusikov, N. V. Gileva]; UDC 658.567.628.47:628.3]

[Abstract] A review is presented of the various means used to remove mercury from industrial wastewater. They include sedimentation, removing mercury as insoluble compounds such as hydroxides, the sulfide or metallic mercury; ion-exchange methods, based on the use of resins such as nitrogen-containing anionites, with the mercury oxidized to the bivalent state by elementary chlorine; adsorption on activated carbon, modified sometimes by complex formers; and reduction with  $\text{NaBH}_4$  or some other reducing agent with subsequent removal of the mercury from the liquid phase by blowing through an inert gas or air. Typical arrangements of equipment for these processes are diagramed and discussed. Figures 3; References 10: 8 Russian, 2 Western.

**Ecological Aspect of Complex Mode-Adjustment Testing of Gas-Combustion Equipment**

937M0082D Kiev *KHIMICHESKAYA TEKHOLOGIYA* in Russian No 2, Mar-Apr 92 pp 77-83

[Article by I. Ya. Sigal, S. A. Parasochka, A. G. Koliyenko, Ye. S. Kernaznitskaya; UDC 662.613.5]

[Abstract] The Ukrainian Environmental Protection Ministry has undertaken an inventory of emissions of oxides of nitrogen into the atmosphere with the goal of establishing standards for harmful emissions. Considering the harmful influence of  $\text{CO}_2$  in the atmosphere and the lack of any consideration of thermal pollution, the authors suggest a study of the possibility of adding carbon dioxide to the list of pollutants, the emission of which is penalized. Combined ecological and heat engineering operating mode adjustment testing should be performed to establish the optimal ecological operating modes of equipment considering process conditions, minimum possible specific heat generation and emission of pollutant substances into the atmosphere. These studies are based on the concentration of harmful impurities, the rate of emission of pollutants, the total emission of pollutants and the specific emission of certain pollutants. If the concentration of pollutants rises above a certain level for a given boiler installation, special measures must be developed and undertaken to reduce pollution. Figures 1; Reference 1: Russian.

**Formation and Methods of Suppression of Toxic Substances When Gas is Used To Roast Green Coffee**937M0082E Kiev *KHIMICHESKAYA**TEKHNOLOGIYA* in Russian No 2, Mar-Apr 92 pp 84-90

[Article by B. M. Krivonogov, N. N. Bazyl, Ye. S. Bibik; UDC 662.613.52:661.982:663.933.4]

[Abstract] When natural gas is used to roast green coffee, toxic substances are formed in the combustion chamber, roasting drum and in the shell cyclone. Each of these three sources of toxic substances has a different set of optimal process conditions to minimize fuel and electric power consumption and produce the best product. Results are presented from studies of the conditions of formation and suppression of toxic substances under these conditions to reduce harmful emissions, maximizing product yield and quality while satisfying ecological requirements. The processes of generation of toxic substances in all three areas of their production are considered. It is found that a roasting unit with recirculation of exhaust gases and oxidative decontamination consumes 34% less thermal energy than a unit without recirculation using a separate furnace for decontamination. Optimal roasting parameters, 260-280°C, 16-17 minutes, maximize product yield, saving about 160,000 rubles per year. Figures 4; Reference 1: Russian.

**Gas-Chromatographic Determination of Certain Toxic Substances in Air and Cable Manufacturing Process Gases**937M0083E Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 47 No 8, Aug 92 pp 1492-1496

[Article by V. V. Larikov, Yu. A. Shurov, O. A. Gogel, Ye. A. Novoselova; UDC 543.42]

[Abstract] The possibility is demonstrated of gas-chromatographic determination of the most important and toxic components in the emissions of machines which enamel electrical conductors. Substances determined include the sum of xylenes, phenol and the sum of cresols. The method can be used to determine pollutants from 6-7 mg/m<sup>3</sup> to 5-7 g/m<sup>3</sup>. It is found that purification of the gases in the first stage of catalytic oxidation is rather effective, with 64-99.5% of the polluting substances removed. The second stage is less effective, eliminating only 1/10 to 2/3 of the residual content. Xylene is most difficult to remove. The most effective

approach to concentrated toxic substances includes separate concentration of phenols on silica gel and aromatic hydrocarbons on polysorb-I or tenax-GC. Figure 1; References 5: Russian.

**Determination of Tetrachlorinated Dibenzo-p-Dioxin, Dibenzofurans and Related Compounds in Commercial 2,4-D Herbicide**937M0083F Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 47 No 8, Aug 92 pp 1497-1503

[Article by Ye. S. Brodskiy, N. A. Klyuyev, V. G. Zhilnikov, N. V. Murenets, B. V. Bocharov, G. L. Rusinov; UDC 543.51:547.621]

[Abstract] A study is made of the content of TCDD, TCDF and related compounds in two specimens of 2,4-D from different production runs at the same chemical plant. The determination is hindered by many other compounds of similar structure, the contents of which are tens or hundreds of times higher than that of the compounds determined. A combination of capillary gas-liquid chromatography and low-resolution mass spectrometry was used to determine the impurity components, with capillary gas-liquid chromatography in combination with high-resolution mass spectrometry in selective detection mode used to identify and determine the isomer composition of the TCDD and TCDF. The total quantity of the compounds determined ranged from 2.6 to 5.9 ng/g for TCDD, 76.0 to 122.1 ng/g for TCDF. The most toxic isomer, 2,3,7,8-tetrachlorodibenzo-p-dioxin was found at 0.10 and 0.002 ng/g in the two specimens. References 9: 2 Russian, 7 Western.

**Analytic Capabilities of "Khimavtomatika" Chromatographic Equipment of Dzerzhinsk Okba for Monitoring of Environmental Pollution**937M0083G Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 47 No 8, Aug 92 pp 1516-1524

[Article by Ya. I. Yashin; UDC 543.54]

[Abstract] This article illustrates the analytic capabilities of gas, liquid and ion chromatographs produced by the Dzerzhinsk OKBA plant for monitoring of ecological objects. The plant has developed and now series produces a system of chromatographic equipment for monitoring of the environment, with both stationary and portable models included. Tables list the equipment manufactured by the plant and methods used to concentrate organic compounds from aqueous specimens. Sample chromatograms are presented. Sample mobile and stationary configurations are presented in chromatographic laboratory for monitoring of environmental pollution is presented. Figures 2; References 6: Russian.

**Wet Rust Traps With Organized Eddy Zones**

937M0084C *Ivanovo IZVESTIYA VYSSHIKH  
UCHEBNYKH ZAVEDENIY: KHIMIYA  
IKHIMICHESKAYA TEKHOLOGIYA in Russian*  
Vol 47 No 6, Jun 92 pp 101-105

[Article by M. P. Sharygin, V. A. Gorbunov; UDC  
621.928.9]

[Abstract] The authors have developed a design for wet dust-trapping equipment with regular mobile packing allowing significant expansion in the area of application of wet dust traps. The equipment has no sprinkler device, features increased free cross section of supporting grid, with 90-98% free space and the oscillation of the packing allows the ejection version of the equipment to be used to cleanse gases with high dust content, yielding highly concentrated solutions. The spray version is preferable for purifying over 200,000 m<sup>3</sup> hr of gases. Design equations are presented for the new equipment. Some 20 sets of the equipment are presently in use, achieving a total economic effectiveness including the ecological factor of 8.8 million rubles. Figures 2.

**Determination of Initial Requirements for  
Standardization and Norms of Emissions of  
Municipal Enterprises With Consideration of  
Data from Observations of Atmospheric Pollution**

937M0090A *Moscow KHIMICHESKAYA  
PROMYSHLENNOST in Russian* No 6 Jun 92  
pp 324-328

[Article by A. S. Belyavskiy]

[Abstract] Initial requirements for determining enterprise emissions were determined by one of 3 variants and these requirements were used to calculate standards of emissions by sources and to establish plant field-standards for enterprises as a whole, which made it convenient to obtain local field-standards for individual buildings, shops or groups of sources of emissions. This approach can be used to achieve a unified strategy of quality control of the atmosphere in the interests of the city as a whole. Programmed complexes were described which ensure optimal quality control of the atmosphere in cities with considerable savings of time and expenses. References 11 (Russian).

**Synthesis of Yttrium, Lanthanum, Neodinium, Praseodymium and Lutecium Alkoxides and Acetylacetonates**

937M0137A Moscow *IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA* in Russian No 11, Nov 92 (manuscript received 5 Dec 91) pp 2490-22493

[Article by V. V. Gavrilenko, L. A. Chekulayeva, I. A. Savitskaya, N. A. Nesmeyanov, Russian Academy of Sciences, Moscow; UDC 547.263:256.4.5;546.31/90]

[Abstract] Metal alkoxides are used as starting reagents in synthesis of various ceramic materials. A simple, laboratory scale synthesis of a number of rare earth metal (REM) alkoxides was reported. The reaction is based on chlorination of REM or their hydrides with anhydrous HCl in corresponding absolute alcohol followed by dehydrohalogenation of the REM-chlorides with equivalent amounts of the alkali metals (Na or Li). In case of methoxide synthesis, metallic lithium was used to dehydrohalogenate the REM-chlorides because the methoxides are insoluble in methanol while LiCl is. Sodium is used with higher alkoxides because NaCl is insoluble in alcohols and the alkoxides are. The separation of solids from the liquid phase is done most effectively by centrifugation. The alkoxides react with acetylacetone to yield

corresponding acetylacetonates. Table 1; references 8: 5 Russian (2 by Western authors), 3 Western.

**Pore Structure and Acid-Base Properties of Amine-Containing Matrices**

937M0138B Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 58 No 11, Nov 92 (manuscript received 22 Jun 92) pp 976-981

[Article by B. V. Zhmud and A. A. Golub, Kiev State University imeni T. G. Shevchenko; UDC 541.183]

[Abstract] Poly(3-aminopropyl) siloxane matrices, having a considerably higher content of functional amino groups than analogous systems of amino silicas, could be used as sorbents or catalyst carriers. However, application requires information on the chemical properties of the ligand coverings of the matrices and other factors which may affect these properties. In the present work a study was made of acid-base properties of poly(3-aminopropyl) siloxane matrices. The change in the apparent protonation constant as a function of the degree of completion of reaction is explained. Also, relationships were found to exist between the magnitudes of macro- and local protonation constants and the pore structure parameters of the matrices. References 9: 8 Russian, 1 Western.

**Determination of Copper Content in Montmorillonite by Electrochemical Methods and Possibility of Regeneration**

937M0092A Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA - KHIMIYA Vol 33 No 3, (manuscript received 26 Nov 91) pp 300-302

[Article by V. F. Yefimova, A. D. Semenova, G. A. Bogdanovskiy and A. V. Areshin; Department of General Chemistry; UDC 541.128.13]

[Abstract] Experimental data characterizing determination of copper content in montmorillonite by reading potentiometric curves of Pt/Pt loading of an electrode in paste prepared from finely ground clay and 1 N  $H_2SO_4$  with addition of a  $CuSO_4$  solution showed a dependence between concentrations of  $Cu^{2+}$  ions in clay and the value of the electro-oxidation current. The study showed the possibility of analyzing the degree of contamination of sands used to remove copper from water and the possibility of their regeneration for repeated use. Figure 1; references 6: 5 Russian; 1 Western.

**Study of Surface of Aluminosilicate Glass Fiber and Some Articles Based on It**

937M0093A Moscow NEORGANICHESKIYE MATERIALY in Russian Vol 28 No 8, Aug 92, (manuscript received 24 Nov 91) pp 1766-1770

[Article by V. S. Kiyko, V. M. Kovylov, Yu. I. Tomilin, V. I. Bukhtiyarov and O. A. Klinov; Uralsk Polytechnical Institute imeni S. M. Kirov; UDC 546.62'284:543.42]

[Abstract] Samples of roll material of aluminosilicate glass fiber mark MKRR-130 and refractory plates mark MKRP-340 and mark MKRPGP-500 were used in a petrographic study on an optical microscope in order to determine the true density and the specific surface of the aluminosilicate glass fiber and refractory plates based on it. The true density of the aluminosilicate glass fiber and articles made from it varied within a range of 2428-2496, depending upon the type of organic bond and of other additives introduced into the fiber during production of articles made from it. The specific surface also changed during this. X-ray phase studies showed a predominantly amorphous structure of the glass fiber and the presence of a crystalline phase probably consisting of elementary silicon or  $SiO_2$ . Determination of the chemical composition and the charge state of elements on the surface showed that the aluminum occurs in the form of  $Al_2O_3$  while the silicon was found to be in a bivalent state ( $SiO$ ) and the elementary form. Figures 2; references 3: 1 Russian; 2 Western.

**Superconducting Properties of Modified Ceramics  $YBa_2Cu_3O_{7-x}$**

937M0093B Moscow NEORGANICHESKIYE MATERIALY in Russian Vol 28 No 8, Aug 92, (manuscript received 5 Jun 91) pp 1776-1780

[Article by G. M. Kaleva, Ye. D. Politova, M. V. Kudinova, S. G. Prutchenko and Yu. N. Venevtsev; Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov; UDC 537.312.62:666.3]

[Abstract] A study of the effect of alloying additives on properties of superconducting ceramics in order to improve the superconducting properties of  $YBa_2Cu_3O_{7-x}$  employed X-ray diffraction analysis, electron microscopy, Mossbauer spectroscopy with consideration of changes of the temperature dependence of the resistivity. Substitution of copper in  $YBa_2Cu_3O_{7-x}$  by Sb, Mn ( $Sb_{1/2}$ ,  $Mn_{1/2}$ ) in a quantity of less than 4% did not worsen the basic superconducting properties. The critical current density increased up to values greater than but almost equal to  $10^3$  A/cm<sup>2</sup> in solid solutions of  $(1-x)Y_{1/2}Ba_{1/2}CuO_{3-x}$  times  $xSr(Sb_{1/2}Mn_{1/2})O_3$  with  $x$  less than but almost equal to 0.04. This was attributed to "purification" of the boundaries and decrease of reorientation capacity of the grains in the growth process. Figures 4; references 15: 3 Russian; 12 Western.

**Synthesis and Properties of Superconducting Ceramics Produced by Use of Rare Earth Concentrates**

937M0093C Moscow NEORGANICHESKIYE MATERIALY in Russian Vol 28 No 8, Aug 92 (manuscript received 24 Sep 91) pp 1781-1785

[Article by L. V. Sazonova, V. A. Krzhizhanovskaya, V. B. Glushkova, A. V. Komarov, S. Kh. Suleymanov and T. N. Baymatov; Institute of Chemistry of Silicates imeni N. V. Grebenshchikova; Russian Academy of Sciences; UDC 666.3]

[Abstract] A study of the synthesis and properties of  $LnBa_2Cu_3O_x$  where Ln is a rare earth concentrate included synthesis of  $YBa_2Cu_3O_x$  used for comparison. Synthesis of  $LnBa_2Cu_3O_x$  (Ln is rare earth concentrate - rare earth-6, rare earth-8) proceeded more quickly than synthesis of  $YBa_2Cu_3O_x$  with formation of a lesser quantity of intermediate products of the reaction. Production of a single phase product required heat treatment at 1220 K.  $LnBa_2Cu_3O_x$  samples synthesized at 1220 K and annealed in air at 770 K had a transition temperature of 81 K in the superconducting state and critical currents of 63 and 120 A/cm<sup>2</sup> at apparent porosity of nearly 20 percent. The sample with rare earth-6 lost superconducting properties at the temperature of liquid nitrogen after prolonged annealing at 670-770 K in an oxygen current. Annealing of sample rare-earth-8 in an oxygen current produced only insignificant increase of the transition temperature in the



superconducting state ( $T_c=83$  K) but increased the critical current up to  $152 \text{ A/cm}^2$ . Figures 5; references 5: 1 Russian; 4 Western.

**Reactions of Aziridine With Di(2-Chloroethyl)Amine in Platinum (II) and Platinum (IV) Complexes. Intra-sphere Synthesis of 1,2-Diaziridine Ethane and its Derivatives**

937M0120A St. Petersburg ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 No 5, May 92 (manuscript received 3 Jan 91) pp 967-971

[Article by S. V. Yakovlev, O. M. Nozdrina, V. B. Ukraintsev, St. Petersburg Technological Institute; UDC 541.49:546.924:546.922]

[Abstract] The goal of this work was to investigate the intra-sphere interaction between aziridine ( $L_1$ ) and di(2-chloroethyl)amine ( $L_2$ ) within the internal sphere of the Pt(II)-Pt(IV) complex. Mixed complexes of Pt(II)-Pt(IV) with  $L_1$  and  $L_2$  were obtained, although no intermediate products could be isolated to identify the individual stages of this transformation. Even though the studied reaction could occur through coordination with Pt(II) or Pt(IV), the intra-sphere reaction between aziridine and 2-chloroethylamine occurred only through a complex formation with Pt(IV), showing that the ligand  $L_2$  exhibits higher alkylating ability than 2-chloroethylamine, probably because of the steric factors. Conditions were identified for the intra-sphere reaction of these ligands leading to the formation of 1,2-diaziridine ethane and its derivatives. References: 7 (Russian).

### Immunotoxicology of Element-Organic Compounds

937M0140A Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 6, Nov-Dec 92 (manuscript received 25 Mar 92) pp 1223- 1229

[Article by D. B. Gelashvili and Ye. B. Romanova; UDC 614.7- 07:612.017.1.014.46]

[Abstract] Widespread use of toxic element-organic and metal-organic compounds in research and industry imposed strict observance of their biological activity, including the effects of these compounds on the immune systems of humans and animals. In the first place, any change in immunological indicators may be an early sign of harmful action of some compound on the organism. Immunological tests often reveal the harmful effects of chemical compounds before they cause visible pathological effects, since their threshold doses are considerably lower than the threshold for systemic effects. Second, disruption of normal immunological processes by chemical compounds enhances an increase in sensitivity of an organism to various infections and allergies. And finally, the high lability of immune systems and the sensitivity of methods for studying immunological reactions makes it possible to obtain supplemental information to aid in understanding the general mechanism of toxicological action of chemical substances. In the present work experimental data are listed on the mechanisms of element-organic compounds on the immune system. Specifically, the immunotoxic and sensitizing properties of alkyl derivatives of Hg, Sn, B, Se, and Te are discussed. References 68: 17 Russian, 51 Western.

### Complexes of Lithium-Organic Compounds and Metal Derivatives

937M0140B Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 6, Nov-Dec 92 (manuscript received 29 Jan 92) pp 1230- 1243

[Article by A. V. Seleznev and M. G. Voronkov; UDC 547.253.4:541.49]

[Abstract] Lithium-organic and lithium-element-organic compounds react with halides and other functional derivatives of metals in three mechanisms. The first is a reduction process, such as in the case of RLi reacting with transition metal salts. In the second, there is an exchange of one or more substituents at the metal atom with a corresponding number of organic or element-organic radicals. The third mechanism includes formation of a complex between the initial reagents. All three mechanisms can take place simultaneously in parallel directions and the reaction products may form complexes either among themselves, or with other components. The present work is a review of information on the complexes of lithium-organic compounds with derivatives of metals, salts of inorganic acids, alkoxides, thiolates, and amides. Attention is focused chiefly on the chemistry of these complexes. References 107: 3 Russian, 104 Western.

### Electrochemical Behavior of Heterometallic Cluster Compounds Containing Mn, Pt, and Fe with Chelate Diphosphine Ligands

937M0140C Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 6, Nov-Dec 92 (manuscript received 19 Mar 91) pp 1244- 1250

[Article by G. V. Burmakina, S. V. Kovalenko, A. A. Ioganson, V. A. Trukhacheva, O. V. Baulina, A. B. Antonova, and A. G. Ginzburg; UDC 541.138:547.1'3:546.711:546.92:546.72]

[Abstract] In a previous work the electrochemical behavior of bi- and tri-nuclear heterometallic cluster compounds containing Mn, Pt and Fe with monodentate phosphorus-containing ligands was studied. The influence of the metal in the ligand on the electrochemical reduction of the cluster was revealed and it was demonstrated that isolobal substitution one of the  $\text{Fe}(\text{CO})_4$  crowns in a tri-nuclear cluster  $\text{Fe}_3(\text{CO})_{12}$  with the electron-rich group  $\text{Pt}(\text{L})(\text{PPh}_3)$  causes a significant shift in the redox potential of the cluster  $(\text{Ph}_3\text{P})(\text{L})\text{PtFe}_3(\text{CO})_8$  to the negative side. It appeared interesting to study the influence of chelate ligands on the electrochemical behavior of heterometallic clusters, since it is known that introduction of a similar ligand to the P atom results in intensifying interaction of Pt and CO. In the present work classical and commutator polarography, cyclic voltamperometry, and controlled potential electrolysis were used to study the redox properties of a number of carbonyldiphosphines. It was demonstrated that the compounds  $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C-CHPh})(\text{P-P})$  and  $[\text{Ph}_2\text{P}(\text{C}_2\text{H}_4)\text{PPh}_2]\text{PtFe}_2(\text{CO})_8$  undergo reverse single-electron reduction. Figures 4; references 10: 5 Russian, 5 Western.

### Monomers and Polymers, Derived by Reactions of Acid Chlorides and Aldehydes With Bivalent Samarium

937M0140D Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 6, Nov-Dec 92 (manuscript received 17 Apr 91) pp 1251- 1254

[Article by N. Ye. Brandukova, Ya. S. Vygodskiy, and S. V. Vinogradova; UDC 546.659:547.1]

[Abstract] Bivalent lanthanide compounds, particularly halogen lanthanides, have unique physical chemical properties. The most interesting is samarium iodide owing to its high redox potential (-1.55 eV) which facilitates rapid and selective reactions with high yields, such as in the reduction of halogen- containing hydrocarbons and tosylates, aldehydes and ketones, nitrocompounds, etc. In the present work a study was made of samarium iodide reactions leading to the formation of new functional aromatic polymers, poly- $\alpha$ -diketones from aromatic dicarboxylic acid chlorides, and polypyridones from aromatic dialdehydes. An effective single stage method was developed for the synthesis of difluorobenzyis by reaction of samarium iodide with o- and p-fluorobenzoic acid chlorides. The resulting monomers

were used in polycondensation processes for the synthesis of new high molecular polyester- $\alpha$ -diketones. References 12: 1 Russian, 11 Western.

**Aliphatic Thiocyanates in Reactions with Grignard Reagents**

937M0140E Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 6, Nov-Dec 92 (manuscript received 27 Jan 92) pp 1364- 1370

[Article by Yu. N. Polivin, R. A. Karakhanov, T. S. Shevel'eva, V. I. Kelarev, and A. A. Bratkov; UDC 542.91]

[Abstract] The reaction of thiocyanates with Grignard reagents at low temperatures may be used to prepare symmetric and asymmetric sulfides. Recently, the reaction of Grignard reagents with isomeric thiocyanates was studied, while reactions of non- isomeric primary aliphatic thiocyanates have not yet been studied thoroughly. In the present work the reaction of butylthiocyanate with RMgX (MeMgI, EtMgI, PrMgCl, iso-PrMgCl, ter-BuMgCl, and PhMgBr) in ether was studied. It was demonstrated that the basic reaction products are dibutyldisulfide, butylalkylsulfide, butylmercaptan, and traces of alkylcyanide. References 14: 4 Russian, 10 Western.

**P-H Carbene Insertion. 4 Communication.  
Formation of O,O-Dimethyl-3-Chloro-  
2-Hydroxypropylphosphonate and  
O,O-Dimethyl-3,3-Dichloro-2-Hydro-  
xypropylphosphonate by Copper Catalyzed  
Atterthor-Todd Reaction**

937M0120B St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 62 No 5, May 92 (manuscript  
received 4 Feb 92) pp 1039-1042

[Article by A. M. Polotov, A. K. Mustafin, Scientific  
Research Chemical Institute imeni A. M. Butlerov,  
Kazan State University; UDC 547.467.2 + 547.241 +  
542.924.4]

[Abstract] The carbene P-H insertion method was used  
effectively in synthesis of various phosphonates. In this  
work an attempt was made to apply this method in  
synthesis of O,O-dialkyl- 3-polychloro-substituted 2-  
ketopropylphosphonates. The starting diazo com-  
pounds: o-polychloro-substituted diazoacetones were  
synthesized as precursors of the carbenes. The reaction  
of o-chlorodiazoacetone with dimethylphosphite pro-  
duced O,O-dimethyl-3-chloro-2-ketopropylphosphonate  
in a 32% yield, b.p. 97-98° C ( $5 \times 10^{-2}$  mm Hg). Similarly,  
o-dichlorodiazoacetone gave O,O-dimethyl-  
3,3-dichloro-2-ketopropylphosphonate, b.p. 95- 100° C  
( $5 \times 10^{-2}$  mm Hg). The reaction of o-trichlorodiazoac-  
etone did not yield the corresponding product evidently  
because of an interfering reduction to the phosphonates.  
The products were characterized by NMR  $^1\text{H}$  and  $^{31}\text{P}$   
and by IR spectroscopy. Heating methyltrichloroacetate  
with a 2-fold molar excess of dimethylphosphite and 10  
mole-% copper-acetylacetonate gave a 21% yield of a  
methyldichloroacetate, b.p. 90° C (100 mm Hg). Refer-  
ences 13: 4 Russian, 9 Western (2 by Russian authors).

**Photoelectronic Spectra and Electronic Structure  
of Organophosphoric Compounds. 5  
Communication. Amino-substituted Compounds of  
Mono-Coordinated Phosphorus (=N-CP)**

937M0120C St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 62 No 5, May 92 (manuscript  
received 12 Nov 91) pp 1043-1046

[Article by V. V. Zverev, Z. S. Ionkin, S. N. Ignatyeva, Z.  
G. Bazhanova, Institute of Organic and Physical Chem-  
istry imeni A. Ye. Arbuzov, Kazan Scientific Center,  
Russian Academy of Sciences; UDC 541.6]

[Abstract] In previous studies it was shown that an  
amine substituent at the carbon atom in phosphoalkenes  
affects the electronic structure of the molecule, lowering  
its energy of ionization and redistributing electronic  
density. In the present work the electronic structure,  
photoelectronic spectra and vertical ionization poten-  
tials of amino-substituted mono-coordinated phos-  
phorus compounds were investigated (=N-C=P). In  
addition, vertical potential of tert-butyl(trimethylsil-  
yl)amine was determined. Comparison of ionization

energies of simple molecules  $\text{P}=\text{C}-\text{Me}$  (I) and tert-  
butyl(trimethylsilyl)amine (II) provided qualitative esti-  
mate of the composition of two outer occupied orbitals  
in the synthesized molecules. In (I), the outer orbital was  
degenerated; it was formed by two mutually perpendic-  
ular  $\pi$ - orbitals:  $\pi_{\text{C}=\text{P}}$  and  $\pi'_{\text{C}=\text{P}}$  which are mixed with  
pseudo- $\pi$ -orbitals of the methyl group. In the test mole-  
cules the degeneration of these orbitals is removed  
because of intensive interaction of  $n_{\text{N}}-\pi_{\text{C}=\text{P}}$ . High effec-  
tiveness of  $n-\pi$ -interaction is the result of the similarity  
in  $\pi_{\text{C}=\text{P}}$  and  $N_{\text{N}}$  orbital energies. Experimentally deter-  
mined data and the calculations based on the model  
 $\text{P}=\text{P}-\text{NMe}_2$  agreed well with each other. Figures 3;  
references 7: 4 Russian, 3 Western.

**Phosphorus Containing Ethylenedithiolates in  
Synthesis of Heterocyclic Compounds**

937M0120D St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 62 No 5, May 92 (manuscript  
received 29 Jan 91) pp 1065-1070

[Article by V. A. Kozlov, Ye. V. Zheltova, L. A. Pok-  
rovskaya, A. F. Grapov, N. N. Melnikov, All Union  
Scientific Research Institute of Chemical Plant Protec-  
tive Agents, Moscow; UDC 547.241]

[Abstract] In continuation of their studies of the syn-  
thesis of phosphorylated vinyl sulfides, alkylation of  
potassium  $\beta$ - diethoxyphosphoryl- $\beta$ -cyanoethyl-  
enedithiolate (I) was investigated using highly reactive  
N-chloromethylphthalimide, 6-chloromethylbenzoxazo-  
line-2-one and 2-chloromethyl-5- chlorothiophene,  
yielding symmetrical  $\beta$ -phosphorylated ketene- S,S-  
acetals. Alkylation of (I) with methyl iodide followed  
shortly by a second equivalent of alkyl halide yielded a  
mixture of geometric isomers which could be separated  
by chromatography on silica:  $\beta$ -diethoxyphosphoryl-  
 $\beta$ -cyano-S-methyl-S-(N- methylphthalimido)keten-  
S,S-acetal. Alkylation of (I) with  $\alpha$ - bromoacetophenone  
yielded 2-mercaptophenacyl-3-diethoxyphosphoryl-  
4-amino-5-benzoylthiophene formed through intramo-  
lecular cyclization. Analogously to its organic analogues,  
(I) undergoes a Mannich reaction with formaldehyde  
and primary amine hydrochlorides yielding 1,3,5-  
dithiazines. Diamines reacted analogously with (I)  
yielding bis-cyclic products. All structures were sup-  
ported by physical-chemical analyses. Table 1; references  
6: 4 Russian (1 by Western authors), 2 Western.

**Extraction of Neptunium (II) Mono- and  
Didentate Neutral Organophosphoric Compounds**

937M0122C St. Petersburg RADIOKHIMIYA in  
Russian Vol 34 No 4, Jul-Aug 92 pp 54-57

[Article by A. M. Rozen, Z. I. Nikolotova, N. A. Karta-  
sheva, I. G. Tananayev; UDC 542.61]

[Abstract] Neptunium (V) is a difficult element to  
extract; the data on its distribution is scarce and

contradictory. In the present work, Np (V) extraction was investigated using carefully purified solvents: TBP, TOPO, carbamoylphosphine oxide ( $\text{Tot}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{CNBu}_2$ , diphosphine dioxide  $\text{Oct}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{POct}_2$ ,  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{PPh}_2$  and  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{PTol}_2$ . The concentration of nitric acid was varied. According to the experimental data obtained in this study, the literature data on extraction with TBP were higher by an order of magnitude.

Characteristic maxima were observed for TOPO and  $\text{Oct}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{POct}_2$ . On the basis of the graphs where distribution coefficients were plotted against water phase acidity, an anomalous aryl reinforcement was observed (increased extraction power of the extracting agent after introduction of an aryl substituent which normally lowered its basicity); this indicated a bidentate coordination of Np (V). Tables 2; figures 3; references: 3 (Russian).



**Phenoxyacetonitriles - Syntones for Preparation of Biologically Active Heterocyclic Compounds**

937M0138E Kiev UKRAINSKIY KHIMICHESKIY  
ZHURNAL in Russian Vol 58 No 11, Nov 92  
(manuscript received 7 May 92) pp 1005-1016

[Article by S. A. Vasilyev and V. P. Khilya, Kiev State  
University imeni T. G. Shevchenko; UDC 547.56]

[Abstract] Chemists and biologists have recently expressed special interest in heterocyclic compounds containing phenoxy groups which includes agents to protect plants from insects as well as pharmaceutical preparations. The present article is a review of published literature on methods of preparation, chemical and biological properties of the title compounds. References 65: 5 Russian, 60 Western.

### Model for Sorption of Organic Substances Dissolved in Water by Porous Copolymers of Styrene and Divinylbenzene

937M0074A Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 14 No 3, Mar 92 (manuscript received 9 Oct 91) pp 163-172

[Article by A. V. Mamchenko, Institute of Colloidal Chemistry and Chemistry of Water imeni A. V. Duman'skiy, Academy of Sciences of Ukraine, Kiev; UDC 541.183]

[Abstract] Along with activated charcoal, porous copolymers of styrene and divinylbenzene are often used in water purification. Many publications have been published on sorption of organic materials dissolved in water but the interpretation of experimental data was usually based on concepts relating to solid structure adsorbents, neglecting the specificity of polymer materials. In the present work an attempt was made to interpret data on sorption of aromatic compounds dissolved in water by styrene-divinylbenzene copolymers. A model was developed for this which considered sorption of substances in cavities formed in the starting sorbent as a result of the swelling of copolymers. An assumption was made that this swelling has a reversible and elastic character and that all newly formed cavities are completely filled with the material being adsorbed. When applied to experimental data, this model, on the whole, described quite adequately the sorption of *p*-chloroaniline and 2,5-dichlorophenol dissolved in water on incompletely relaxed samples of styrene and divinylbenzene copolymers which contained 10 and 30% of a crosslinking agent in the starting monomer mixture. Table 1; figures 2; references 16: 11 Russian, 5 Western.

### Membrane Gas Distribution. 5. Polymer Membrane Materials

937M0082B Kiev *KHIMICHESKAYA TEKHOLOGIYA* in Russian No 2, Mar-Apr 92 pp 19-32

[Article by V. L. Saprykin; UDC 678.06:62-278:66.067.2.38]

[Abstract] This review of the [primarily Western] literature discusses the use of polymer membrane materials in gas distribution. Specifically, the developments of Monsanto Corporation in manufacture and modification of gas distribution membranes is discussed at length. A number of Monsanto patents relating to modification of membranes by acid and base treatment of polymer materials are cited. Solvent and polyphosphazene methods are also mentioned. The development of asymmetrical hyperfiltration membranes in the 1960's, it is reported, allowed a qualitatively new level of solution of the problem of increasing the speed of filtration. References 49: 5 Russian, 44 Western.

### Nonisothermal Thermogravimetric Analysis in Study of Destruction of Polymers and Possibility of Stabilization

937M0084A Ivanovo *IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA IKHIMICHESKAYA TEKHOLOGIYA* in Russian Vol 47 No 6, Jun 92 pp 3-15

[Article by G. N. Smirnova; UDC 541.64:542.978:547.979.733]

[Abstract] This review of the Russian and (primarily) Western literature systematizes recent (1982-1990) works on thermogravimetric analysis, widely used in the nonisothermal variant to determine the kinetic parameters of destruction processes and particularly the effective activation energy. Most of the articles reviewed propose the use of the berivatograph to study processes of polymer destruction, sometimes in combination with other instruments. Polyvinyl chloride, polyoliphens and other polymers are discussed. References 41: 8 Russian, 33 Western.

### Mass Transfer From Solid Phase Through Insoluble Polymer Coating

937M0089A Moscow *TEORETICHESKIYE OSNOVY KHIMICHESKOY TEKHOLOGII* in Russian Vol 26 No 4, Jul-Aug 92 (manuscript received 10 May 90) pp 510-515

[Article by Ya. M. Gumnitskiy, I. M. Fedin, K. F. Al'-Alusi and I. A. Demchuk; L'vov Polytechnical Institute, L'vov Medical Institute; UDC 532.73+539.21]

[Abstract] Continuation of a study of the kinetics of liberation of active components from particles coated with a water-insoluble polymer coating utilized a mathematical model of mass transfer from the solid phase of a substance from capsulized particles through water-insoluble polymer coatings. The mechanism of the process of liberation proceeded in 3 stages: 1-impregnation of the polymer film by the solvent, dissolution of the solid phase and diffusion of particles of the component through the film, 2- dissolution of the solid phase, transfer of the component to the surface of the film and into the surrounding solution and 3- mass transfer of the dissolved component. Exact and approximate analytical solutions of equations of the model were found. Experimental data confirmed the analytical solutions. Figures 3; references 10: 9 Russian; 1 Western.

### Synthesis of ion Exchange Membranes by Radiation Grafting Polymerization of Acrylic Acid on Polyethylene Films

937M0115B St. Petersburg *ZHURNAL PRIKLADNOY KHIMII* in Russian Vol 65 No 3, Mar 92 (manuscript received 5 Jul 91) pp 617-624

[Article by A. P. Polikarpov, Institute of Physical Organic Chemistry, Academy of Sciences of Belarus; UDC 541(64 + 15):547.371]

[Abstract] Radiation grafting polymerization of acrylic acid on polyethylene films along with its homopolymerization was studied using direct irradiation of polyethylene in aqueous solution of its monomer. The distribution of grafted polyacrylic acid in polyethylene film was studied as a function of the conditions of the grafting process. Grafting acrylic acid on polyethylene affects its sorption ability: a decrease in diffusion coefficient and a considerable increase in the equilibrium sorption are noted. This facilitates localization of the graft in film layers close to the surface in water solution based runs. With a constant concentration of Moore salt, the quantity of polyacrylic acid increases with increased radiation dose. The degree of acrylic acid grafting expressed as a function of the concentration of Moore salt on films of different thickness show an extremal character. This is related to the competing reactions in the system, those of homo- and grafting polymerization with different levels of the inhibitor in the amorphous phase of polyethylene and in solution. The data obtained could be used in selecting optimal reaction conditions for the synthesis of carboxyl containing ion exchange grafted copolymers based on polyethylene. To obtain electricity conducting ion exchange members, thin films and water solutions of acrylic acid must be used with a 30-50% concentration of the monomer and at least a 0.4% concentration of Moore salt. Table 1; figures 5; references 19: 13 Russian (2 by Western authors), 6 Western.

**Reactions of Zirconocene Hydride with Polybutadiene. Synthesis of Zirconium-Containing Polymers**

937M0140F Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 6, Nov-Dec 92 (manuscript received 29 Nov 91) pp 1386- 1390

[Article by Ye. Yu. Baukova, L. M. Bronshteyn, P. M. Valetskiy, M. G. Yezernitskaya, B. V. Lokshin, L. I. Strunkina, O. M. Mikhaylova, M. Kh. Minacheva, and V. B. Shur; UDC 541.49:547.1'13:546.831]

[Abstract] Hydrozirconation of olefins and acetylenes is used widely to prepare new zirconium-organic compounds and other preparative syntheses. The zirconizing agent normally used is zirconocene chlorohydride (Schwartz reagent). Reactions have also been reported between acetylenes and zirconocene dihydride. In the present work polydibutadiene was treated with  $\text{Cp}_2\text{ZrH}_2$  and  $\text{Cp}_2\text{Zr}(\text{Cl})\text{H}$  to synthesize new polymers containing  $\delta$ -bound  $\text{ZrCp}_2$  groups. Spectral investigation of the products resulting from reaction of polybutadiene with  $\text{Cp}_2\text{ZrD}_2$  and  $\text{Cp}_2\text{Zr}(\text{Cl})\text{D}$  demonstrated that polybutylene does not react with  $\text{Cp}_2\text{ZrH}_2$  by hydrozirconation, while  $\text{Cp}_2\text{Zr}(\text{Cl})\text{H}$  reacts at the polyethylene double bond via a hydrozirconation mechanism. References 12: 4 Russian, 8 Western.

**Kinetics of Oxidation-Reduction Reactions of U, Np and Pu in TBP Solutions. 4 Communication. Reduction of Np(VI) in Nitrous Acid**

937M0122A St. Petersburg *RADIOKHIMIYA* in Russian Vol 34 No 4, Jul-Aug 92 pp 28-34

[Article by V. S. Koltunov, K. M. Frolov, M. Yu. Sinev, Yu. V. Isayev; UDC 546.799.3]

[Abstract] The authors reported earlier that  $\text{HNO}_2$  reduction of Np(VI) in a nitric acid solution of TBP does not take place and that reduction of Np(VI) and oxidation of Np(V) in hydrochloric acid solution occur at identical rates resulting in an equilibrium which shifts towards the formation of Np(V) when the acidity of TBP is lowered. The goal of the present work was to establish kinetic mechanisms of Np(VI) reactions with  $\text{HNO}_2$  in hydrochloric acid solutions of TBP. Only two valence forms of neptunium were found in the reaction medium Np(VI) and Np(V); Np(IV) was absent. This may indicate an insignificant role of the disproportionation of Np(V) under the reaction conditions used. Other data showed that reduction of Np(VI) by nitrous acid is proportional to the concentration of  $\text{HNO}_2$  and inversely proportional to the concentration of  $\text{HClO}_4$ . Water concentration in TBP did not seem to have any effect on this reaction nor did the dilution of TBP with benzene. The activation energy for reduction of Np(VI) is 2.5-fold lower than the activation energy of the oxidation of Np(V) and therefore, with temperature increase, the equilibrium of this reaction will shift towards formation of Np(VI). An assumption was made that the limiting step in reduction of Np(VI) is the slow reaction of the  $\text{NpO}_2(\text{ClO}_4)_2 \cdot 2\text{TBP}$  complex with nitrite ions, the concentration of which is reversibly proportional to the acidity of the solution. Tables 2; figures 2; references 7: 6 Russian, 1 Western.

**Extraction Characteristics of Palladium Mono- and Bineutral Organophosphoric Compounds**

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[Article by A. M. Rozen, Z. I. Nikolotova, N. A. Kartasheva; UDC 542.61]

[Abstract] Extraction of micro quantities of Pd (II) was investigated using three monodentate organophosphoric compounds: TBP, TIAP, TOPO and three didentate ones:  $\text{Oct}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{POct}_2$ ,  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{PTol}_2$  and  $\text{To}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{PCNBu}_2$ . Experimental values obtained were compared with literature data showing that varying the acidity, the distribution coefficient maximum for palladium did not correspond to the generally accepted view of a complete dissociation of  $\text{Pd}(\text{NO}_3)_2$ . The shift of this maximum towards lower acidity could be due to the fact that palladium in the water phase exists as the ion  $\text{PdNO}_3^+$ . Due to the fact that no aryl reinforcement was noted in extraction with

didentate extracting agents, a conclusion was reached that the coordination was monodentate. Figures 4; references: 3 (Russian).

**Method of Measuring Activity of -Emitting Nuclides on Aerosol Filters**

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[Article by V. P. Ignatov, V. N. Galkina; UDC 541.182.2/3:543.52:546.79]

[Abstract] The ability to use inorganic luminophore zinc sulfide in a scintillation method to determine activity of  $\alpha$ -emitting nuclides in preparations obtained from aerosol filters dissolved in organic solvent was investigated. This method consists of dissolving the filter, adding the luminophore, drying the sample and determining the radionuclide activity. The effectiveness of the registration of  $\alpha$ -emission was studied as a function of the content of luminophore, the filter material, the stained and colorless substances isolated from the analyzed preparations, etc. The effectiveness of  $\alpha$ -emission registration was not affected by the filter material or by the solvent used (acetone, chloroform or toluene). This method appeared to be effective in determining  $\alpha$ -emission of nuclides on aerosol filters without having to use any correction coefficients. Table 1; figures 3; references 10: 5 Russian, 5 Western.

**Mathematical Modelling of Radiation Chemical Processes in Nitrous Acid Solutions of Plutonium. 2 Communication. Accumulation of  $\text{HNO}_2$  in Plutonium Solutions**

937M0122F St. Petersburg *RADIOKHIMIYA* in Russian Vol 34 No 4, Jul-Aug 92 (manuscript received 1 Apr 91) pp 91-100

[Article by M. V. Vladimirova, Ye. A. Golub; UDC 621.039]

[Abstract] Kinetics of the accumulation of  $\text{HNO}_2$  in 3 and 6 molar  $\text{HNO}_3$  during radiolysis in plutonium solution was studied using mathematical modelling. Nitrous acid forms during hydrolysis of  $\text{NO}_2$  radicals resulting from irradiation of  $\text{NO}_3^-$  ions and the  $\text{HNO}_3$  molecule. Calculations were performed assuming presence and absence of plutonium, using corrected values for the radiation-chemical yields of  $e_{aq}^-$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{OH}$  and  $\text{H}_2\text{O}_2$ . Regardless of the presence or absence of plutonium the yield of  $\text{HNO}_2$  was practically the same, only the kinetics of its accumulation varied somewhat. The effect of various factors on the accumulation of  $\text{HNO}_2$  was evaluated and the calculated data were compared with experimental findings. The rate constant of thermochemical breakdown of nitrous acid was determined. Tables 4; figures 4; references: 4 (Russian).

**Spectroscopical Investigation of Glass-Composition Materials for Immobilization of Radioactive Waste**

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[Article by S. V. Stefanovskiy, M. I. Ozhovan, O. K. Karlina; UDC 621.039.73:66.018.86.666.1]

[Abstract] The goal of this work was to investigate glass composition materials based on boron silicate glass containing various sulfate components by EPR and IR spectroscopic methods. It was shown that paramagnetic centers connected with sulfates are formed in these glass composition materials along with paramagnetic centers characteristic of irradiated boron-silicate glass. Mechanical dispersion of sulfates in the matrix of boron silicate glass yields a product with coexistence of phases resembling the starting phases. Dispersion of  $\text{BaSO}_4$  in boron silicate glass and  $\text{CaSO}_4$  in glass containing zinc and lead oxide, results in a slight change of the phases on account of the transition of a portion of cationic component of the dispersed phase into the glass matrix. Tables 2; figures 4; references 13: 10 Russian (1 by Western authors), 3 Western.

**Nuclear-Physical Characteristics of Hot Particles Formed as a Result of Chernobyl Nuclear Power Station Accident**

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[Article by N. A. Loshchilov, V. A. Kashparov, V. D. Polyakov, Ye. B. Yudin, V. P. Protsak, M. A. Zhurba, Z. Ye. Parshakov; UDC 546.2295+621.039.542]

[Abstract] From the very beginning of Chernobyl release radionuclides, microscopic particles were noticed with high specific activity - the so called "hot particles" (HP). Other HP resulted from condensation of volatile radionuclides on soot, dust and construction material particles. The latter showed low specific activity and are primarily surface concentrated. The behavior of condensed HP resembles the behavior of released radionuclides observed after various A-bomb tests; the behavior of fuel HP, concentrated in a narrower zone and containing the principal mass of biologically significant

radionuclides, has not been adequately studied to this time.  $\gamma$ -Spectrometric and radiochemical analyses of the radionuclide content of 1200 samples of HP collected during 1987-1989 years was carried out. The bulk of the analyzed material (97%) showed radionuclide composition similar to the nuclear fuel of the 4th block at the time of the accident:  $^{95}\text{Zr}$ ,  $^{95}\text{Nb}$ ,  $^{103,106}\text{Ru}$ ,  $^{125}\text{Sb}$ ,  $^{134,137}\text{Cs}$ ,  $^{144}\text{Ce}$ ,  $^{154,155}\text{Eu}$ ,  $^{241}\text{Am}$ . The  $\alpha$ -activity of each HP sample was determined showing presence of  $^{238,239+240,241}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242,243+244}\text{Cu}$ . The extent of the burn-out was determined ranging from 0.8 to 15.2 MWatt-day/kg; the most probable value for the fuel HP was thought to be in the range of 8-11 MWatt-day/kg (the basic composition of the fuel showed that extent of the burn-out was 14 MWatt-day/kg). Figures 3; references 20: 8 Russian, 12 Western (1 by Russian authors).

**Classification of Radioactive Fall-Out in South-Eastern Direction From Chernobyl Nuclear Power Station**

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[Article by Yu. V. Dubasov, A. S. Krivokhatskiy, N. N. Khramov; UDC 502:621.039:519.237]

[Abstract] Statistical classification methods are widely used in social and biological sciences; in chemistry they were introduced only during the past 30 years. At present a lot of experimental data exist on radioactive contamination of large territory resulting from the Chernobyl accident which needs classification and processing to establish accurately the volume of emitted radionuclides. It was decided to show that statistical classification methods can be used for this purpose, employing cluster, factorial and discriminant methods of analysis. The radionuclide content in soil was analyzed from the zone of possible reevacuation in the south-eastern direction from Chernobyl. The following nuclides were determined:  $^{134,137}\text{Cs}$ ,  $^{141,144}\text{Ce}$ ,  $^{238,239+240}\text{Pu}$ ,  $^{140}\text{Ba}$ ,  $^{103,106}\text{Ru}$ ,  $^{95}\text{Zr}$ ,  $^{131}\text{I}$ ,  $^{242}\text{Cu}$ . The analytical methods used for classifying the contamination have not been used properly thus far, but the seriousness of the problem will bring them into a much wider use. In a general case, this classification will permit identification of the sources and their contribution to the contamination process. Table 1; figures 2; references 5: 3 Russian (2 by Western authors), 2 Western.



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